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Evaluation of Flocculation, Sedimentation, and Filtration for Dewatering of Algal Biomass

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EVALUATION OF FLOCCULATION, SEDIMENTATION, AND FILTRATION FOR DEWATERING OF ALGAL BIOMASS

THESIS

A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science in
Biosystems and Agricultural Engineering
in the College of Engineering at the University of Kentucky

By

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Lexington, Kentucky

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Lexington, Kentucky

2016

ABSTRACT OF THESIS

EVALUATION OF FLOCCULATION, SEDIMENTATION, AND FILTRATION BY FOR DEWATERING OF ALGAL BIOMASS

Algae can be used as a feedstock for agricultural fertilizers, livestock/poultry feeds, anaerobic digestion, and biofuel production. Regardless of the end product, water removal is necessary and difficult to do cost effectively. For each product the requirements for moisture content (or solids content) vary, such that a desirable water removal strategy would need to be adaptable to varying levels of water removal. Flocculation, with sedimentation and drying was evaluated as a possible strategy for algae dewatering. Anionic and nonionic flocculants are known to be ineffective at flocculating algal culture, which was confirmed for this case by electro-osmotic flow testing of the algae and jar tests with three flocculant charge types. Electrophoretic mobility of the algae indicated that it has a negative charge and no flocs were present in the jars. The effectiveness of the cationic flocculant was determined by measuring settling rates, supernatant turbidity, and filtration rates. Sedimentation and filtration rates of *Scenedesmus acutus* were measured with varying dosages (0-25 ppm) of a synthetic cationic polymeric flocculant. The results of this study should assist in predicting the time it takes to thicken algae at a concentration range of 0.4-1.0 g/L to a product at a concentration range of 15-250 g/L.

KEYWORDS: algae, flocculation, filtration, dewatering, thickening, sedimentation

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April 29, 2016

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CHAPTER 1 INTRODUCTION

Carbon dioxide is associated with global warming and was investigated for its risk to public health along with five other greenhouse gases (GHG) through the Clean Air Act Section 202(a) (EPA 2009). Coal-fired power plants in the United States emitted 1827.3 million metric tons of CO_2 in 2011 (EIA 2012). Hence, there is motivation to reduce the amount of CO_2 emitted from coal-fired power plants. Interest in algae potential is also motivated by carbon credits. The biomass collected from algae processes might be able to enter relatable product markets for energy, feed stock, raw materials, and so forth (Mata et al. 2010).

Algae can be utilized to fix carbon dioxide from flue gas streams after coal combustion, mitigating the release of CO_2 to the environment. Since they are phototrophic, algae can convert carbon dioxide into organic compounds such as saccharides and lipids. These compounds generate interest within the scientific community due to their utilization opportunities as a fuel or co-product. Algae solids can be thickened into slurry that can be fed to anaerobic digestors as a feed for methanogens. The solids could also be dried completely for processes such as pyrolysis. If the water used for cultivation is considered useful in digestion, then possibly slurry, 2-5 wt%, can be added. If this free water needs to be removed, the solids concentration can be reduced to 10-15 wt% range with most mechanical separation techniques. Other techniques must be utilized to remove more moisture. An algae product with no free water usually yields a 25-30 wt% cake for most microalgae strains. In oil upgrading for example, lipids could be extracted from the algae biomass to be converted to biodiesel and sugars could be fermented to ethanol with wet or dry extraction techniques. Mechanically removing water avoids the intensive energy required for evaporation, which is an extreme cost for drying a very dilute suspension of algae cells. For those products that can be utilized in a wet form, the biomass can be conditioned to meet specifications. Removing the necessary amount of free water can reduce drying and transportation costs.

Algae could have the potential to remove millions of tons of CO_2 from flue gas, but that would only be a fraction of national emissions. In order to remove a significant portion of the greenhouse gas, huge volumes are required. Several ten-thousand hectares of algae ponds would be required to mitigate over one million tons of CO_2 (Benemann 1997). The 1,797 MMT of CO_2 was generated from coal powered energy in 1997 and 2,101 MMT of CO_2 altogether (EPA 2012). The reduction of emissions in recent history is due to closing of older coal units, however the demand for electricity will most certainly increase in the future and require more tons of coal to be consumed to meet the demand (EIA 2010). For the estimate of one MMT mitigation with algae ponds at a one meter depth, 10,000 hectares yields 10,000,000 kiloliters of dilute biomass that would need harvesting on a weekly if not daily basis depending upon growth rate. Therefore swift, simple methods must be executed to manage this large amount of water.

1.1 Current uses of algae

There are many products that are derived from algae. Many species have been used as a food source, nutritional supplement, food additive, pharmaceutical, cosmetic, animal

feed, and have potential as biofuel/energy (Pulz and Gross 2004). Kelp, brown algae, is a vibrant ingredient in Asian cuisine. Compounds such as β-carotene can be extracted for vitamins. Some strains of microalgae may contain elevated concentrations of polysaccharides, proteins, or lipids. They may be processed for different applications, depending on which organic compounds are present. Many systems, ponds and PBRs, require nutrient addition for algae growth. Similarly to plant-based phototrophic organisms, algae need both primary macronutrients and micronutrients. Algae research has taken place for a lengthy amount of time; much research has been done in the 1950s and continues in more recent investigation. Nutritional requirements of the algae have been assessed for maximum growth rates (Kratz and Myers 1955). Above all nitrogen, phosphorus, and potassium are primary necessities, while calcium, sulfur, magnesium, chelates, etc. are secondary requirements. Other trace elements and even salts are required by the algae in accordance with Liebig's law of the minimum. On smaller scales, these compounds can be added in purer forms of laboratory chemicals such as urea. But on larger scales urea and other elements can be attained in agricultural fertilizers which contain filler material. Since the algae cells and free solution contain amounts of the added nutrients, a market might exist for microalgae as a liquid fertilizer. Farmers could spray the mixture directly from an algae culturing reactor at its growing concentration (up to 1 g/L). A dry product could even be spread onto fields, adding elemental nutrients as well as organic matter. Some strains produce natural polysaccharides like agar and alginates used for food and microbiology because of their gelling characteristics (Pulz and Gross 2004). Another organic compound found in algae is protein which varies in composition depending on culture species. Animals produced for the food industry usually required high protein diets. Fish naturally eat different forms of algae. Various livestock diets could incorporate dry algae feed with high-protein, high-carbohydrate, or high-lipid contents. In some cases including *Chlorella*, *Scenedesmus*, and *Spirulina* cultures, the carotenoids in the chlorophyll acts as an antioxidant to boost the immune system of animals (Pulz and Gross 2004). Algae in general are nutritious to many other organisms; whether they are humans, plants, animals, or even bacteria.

Algae are now being examined as a feedstock for fuel alternatives (Li et al. 2008). There is much interest in implementing algae as a new "green" energy source. Many strains contain vast compositions of all basic organic molecules and compounds, which can be used for an array of various chemicals (Noue and Pauw 1988). Lipids could be extracted, via wet or dry milling, and further processed into bio-oil. This bio-oil can be upgraded as a diesel alternative or combusted for steam generation. Dry algal biomass can be pyrolyzed or gasified to produce bio-gas. Depending on the operating conditions, gasification may yield diverse quantities of gases, liquids, or chars. The gases would be co-fired with natural gas. Carbohydrate producing strains may be joined as a sugar starter with yeast in ethanol fermentation (Chen et al. 1998). Methanogens produce methane gas by breaking down organic matter, algae, through anaerobic digestion.

The concept of algae as a feedstock for alternative fuel sources and also as mitigation for CO_2 has the potential to address many energy and environmental problems. However, challenges with harvesting and collecting algal biomass must be surmounted. Dewatering and thickening processes are a major hindrance in employing algae systems. Thickening means that the viscosity of a substance is increased by some means of

water/liquid removal. Dewatering is the removal of water from solids in a mixture by these and other types of wet classification. However, these terms are somewhat interchangeable.

For large amounts of CO_2 mitigation, consequentially large amounts of algae must be grown. That algal biomass will need to be harvested continuously to maintain an operating system. Algae is said to be harvested whenever the dilute suspension of 0.02-0.06% TSS (total suspended solids) is collected and then conditioned to 5-25% TSS or higher (Shelef et al. 1984). Processes downstream demand only the algal biomass and not the huge volume of water that follows.

Since there is such a large burden to remove water from algal biomass, one technology suggested is flocculation to facilitate removal of algae from suspension. This process actually makes the cells susceptible to other handling techniques. Using some secondary thickening process is required for higher solids. Thickening equipment under speculation is centrifugation, pressure filtration, vacuum filtration, flotation, and many more.

1.2 Objectives

The rationale behind this thesis is to better understand techniques that can dewater and thicken algal biomass. While there are many processes that could be utilized (reviewed in Chapter 2), flocculation with sedimentation and filtration were selected because they are standard thickening processes that are used in commercial applications, such as wastewater treatment and mineral processing. Flocculation and sedimentation are needed to collect the cells for further conditioning. Filtration is practiced commercially on particles of similar size but much heavier densities. The goal of this work is to evaluate the time and processing conditions that would be required for thickening processes using these methods for obtaining various final concentrations (based on the requirements for end-use). These conditions could aid in establishing sedimentation/filtration rates and therefore confirm the plausibility of using these standard industrial techniques to dewater algal biomass. The specific objectives are as follows:

1. Selection of the optimal flocculant to be use with the specific algae of interest, *Scenedesmus acutus* (Chapter 3).

2. Evaluation of the performance of the optimal flocculant via sedimentation (Chapter 3).

3. Evaluation of the performance of a filtration step after sedimentation (Chapter 4).

CHAPTER 2 EXTENDED BACKGROUND

There are many techniques for solid-liquid separation, where quite a few are performed in wastewater treatment or mineral processing. In these applications, the particles are denser than water, where the cells are rigid and spherical. Algae particles have a specific weight near 1.0 with malleable cells walls resisting mechanical and even chemical separation practices. Since most culturing systems can promote concentrations between 0.4-3 g/L, a tremendous portion of the water must be separated from algal solids to produce a suitable product. Solids content required depends on the end-use of the product. Some products are desired as a liquid, others as slurry or paste, and others entirely dry. These products can be supplied by cost-effective and emission-limiting mechanical dewatering.

2.1 Flocculation

Flocculation is widely used to facilitate the removal of suspended solids. The solids are extremely small, making filtration difficult. Basic mechanics of flocculation are based on electro-kinetics to attract particles or cells, towards one another. Flocs are formed when multiple cells agglomerate (Figure 2.1). The flocs can grow depending on conditions. Continuously stirring the mixture causes collisions which allow ionic bonds to occur. These collisions can also occur by Brownian motion, where the original cells are held in suspension, flocs can fall out of solution. Depending on the new characteristics of the flocs, density and size in particular, they can be handled more efficiently by subsequent dewatering processes.

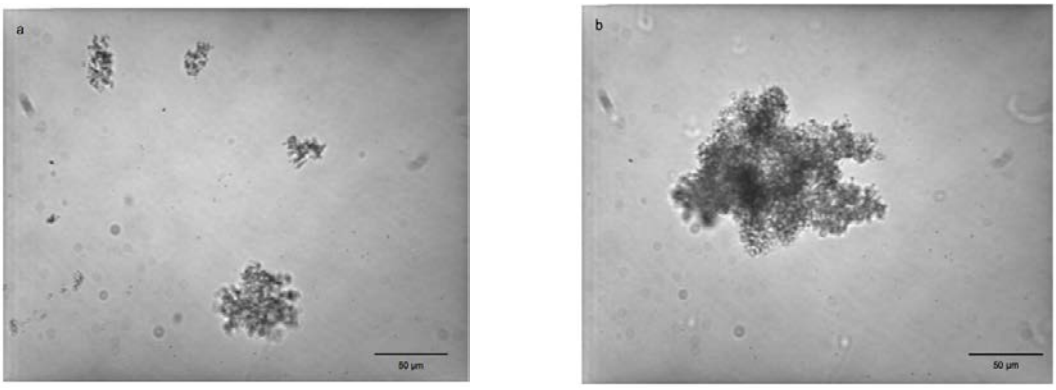

Figure 2.1 Examples of floc growth after mixing; left: 5 min, right: 10 min (Spicer et al. 1996).

There are many methods to flocculate algae. High pH levels can cause precipitation of calcium or magnesium salts (Vandamme et al. 2012). Since salts are nonionic, the crystalline structure rearranges at higher pH ranges. In magnesium hydroxide, the bivalent cations of magnesium are replaced by trivalent iron or aluminum. Regardless of the circumstances, there is charge neutralization. Negative algal cells are attracted to the positive outer layer of the salt compounds. The only addition would be the cations, anions, or entire compounds needed to make appropriate salts. Charge neutralization can also be achieved by lowering the pH. Once there are decreased electrostatic forces acting

on the cells, they can be pulled out of solution by gravity. However, the extreme pH levels could be harmful to the health of the algae.

Other methods include the use of flocculants. Flocculants are chemicals used to remove turbid solids from a solution. They are very dependable for commercial uses such as waste water treatment and mineral processing. When properly used, they have extremely high capture efficiency. Settling rates can be very high, and the effects of pH are usually minor. However, some flocculant types have better activity in particular pH ranges. Some are even food-grade and pose no threat to human or environmental safety. Their reliability and ease of application make them a prime candidate for algae solid-liquid separation. There are many different types of flocculants which will be further discussed in section 2.1.2.

2.1.1 Algae electro-kinetics

Literature shows that microalgae are typically negative within normal pH ranges and can be confirmed by conducting electrophoresis on a sample (Udumane et al. 2010). Algae cells are roughly 5 µm and have a specific gravity near one, because the cell contains about 70-80% water. Since the cells have relatively low mass, steric effects keep them suspended where Van der Waals forces balance against gravitational forces. In surface chemistry, the electric double layer influences the interactions among components in solution. Cations will attract most microalgae strains, which can be explained by the double layer model. The Helmholtz layer contains oppositely charged ions. Gouy and Chapman later discovered that there is diffuse layer carrying the same charge demonstrated in Figure 2.2 (Shamlou 1993). If there were another large particle in solution that was positively charged, then the diffuse layer would attract the two particles.

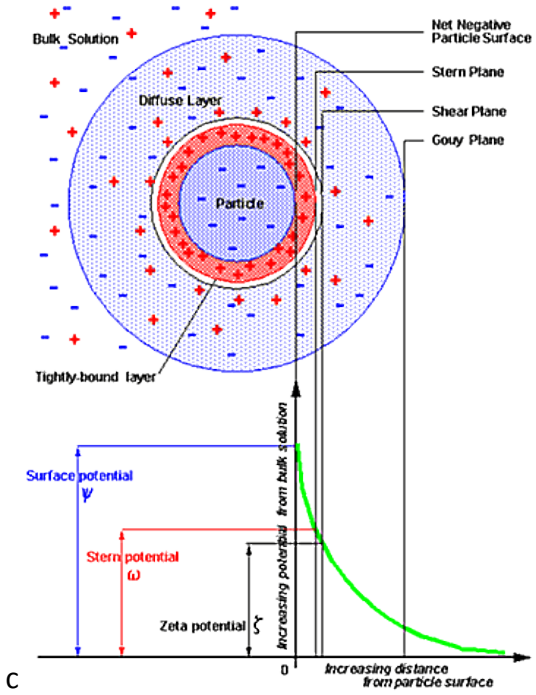

Figure 2.2: Electro-kinetics of particles in solution, showing the double layer model and the relationship to the zeta potential (Shamlou 1993).

If enough energy is applied, then bonds can occur between oppositely charged particles. Before the bond, there are interactions that take place within a small distance of the particle surface. A routine means of measuring the charge of a particle is by electrophoresis. The zeta potential, seen in Figure 2.2, can be determined by flow through a charged solution. It is a measurement of the electro-kinetic potential of a colloidal suspension. At higher zeta potentials, usually measured in mV, particles are more stable as they repel one another. This technique is known as electro-osmotic flow. Within the Gouy plane, closer to the particle, more oppositely charged ions surround the inner layer. The diffuse layer gives insight to the properties of the particle, such as charge type and charge intensity.

The mechanics of flocculation occur on both microscopic and macroscopic levels. Flocculant products, whether dry or liquid, are tightly bound polymers formed by crosslinking hydrogen bonds. When water is introduced, the polymer begins to unfold. Any portion of the flocculant that has not bonded with an oppositely charged ion is termed an active site. When colloids adhere to the active site, they tend to attract active sites on the same polymer or different polymers. This interaction is bridging, which is vital to floc growth. From a macroscopic scale, the flocs are larger when more bridging occurs. Bridging and ionic bonding of the active sites only occur by collision frequency. Low shear mixing initiates more polymer-particle and floc-floc collisions. Brownian motion can create collisions, but at a slower rate. High shear mixing can cause floc breakage (Stechemesser and Dobias 2005). In Figure 2.3, polymer is added to water to instigate hydrolysis that unfolds the polymer chain. A cationic flocculant will attract negative particles which will bind to active sites on the monomer units. Multiple polymers eventually bridge to grow flocs, especially with mixing.

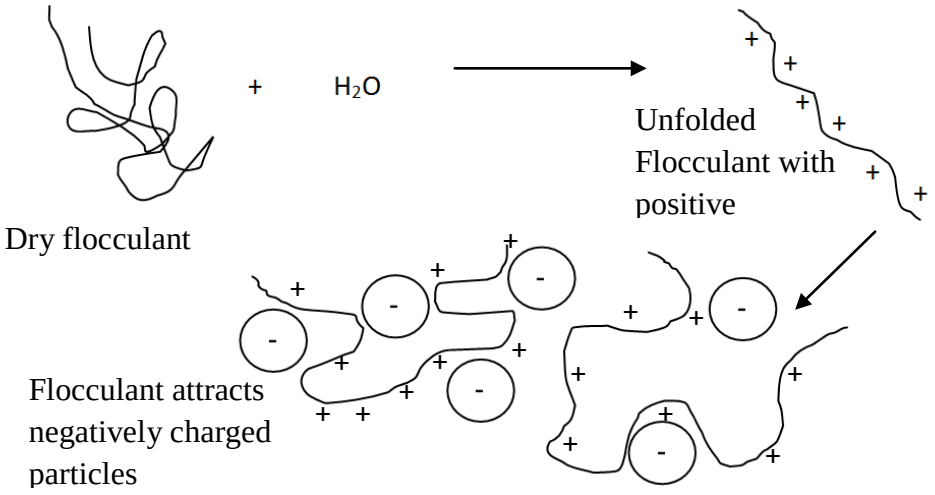

Figure 2.3: Top: Shows the unfolding of a cationic polymer and bottom: attraction of negative particles with bridging affects (based on Stechemesser and Dobias 2005).

2.1.2 Flocculant types

There are many different types of flocculants, but most behave similarly in that they are long chain polymers with elevated charge intensity. They can be divided into two separate types, natural and synthetic. There are three main groups; cationic, nonionic,

and anionic. All three groups can be categorized by molecular weight, roughly translating the length of the polymer. A charge density is associated with the cationics and anionics. In the commercial market, charge density will be scaled over 0-100%. This is generalized by the ratio of *charged mass/total mass*.

Some speculation has surfaced in the use of alum for algal flocculation. This is an inorganic mineral composed of aluminum sulfate. It has been very widely used in water clarification for many years. Alum is typically formed when bauxite is calcined, or heated to drive off bound water molecules. The aluminum ore, bauxite, is a mineral rock that is mined from deposits underground. Having slow reaction kinetics, alum is usually added in large concentrations to create substantial flocs. The capture efficiency can vary greatly. Since water clarity is the most important aspect of flocculation in waste water treatment, a chemical or selection of chemicals must remove a substantial amount of suspended solids. Loading of heavy metals, via aluminum, into water systems became precarious. Treatment facilities began to turn their focus to other chemicals.

Another natural flocculant that is under consideration is chitosan. It can be formed by applying sodium hydroxide or another alkali solution to crustacean shells that contain high levels of chitin. The process of dissolving these hard cellulosic structure is called deacetylation. Chitosan can be used in wide variety of products such as dietary supplements, cosmetics, pharmaceuticals, and flocculants. Chitin and chitosan are very basic and have molecular weights of 1-2.5 million and 0.1-0.5 million respectively (Kumar 2000). While chitosan is a long chain polysaccharide, even longer chained polymers are more effective at bridging, therefore creating large flocs. Its performance is very similar to alum. Since it is only sugar, there isn't any harmful effect to the algae, and the algal cells are able to be grown in media after flocculation (Divakaran and Pillai 2001).

Polyelectrolyte flocculants are one of the newest lines of chemicals used in water treatment. In the late 1970's and early 1980's, a transition began to emerge: polyelectrolytes began to be widely used throughout wastewater treatment (Vernick and Walker 1981). They are often used in current treatment systems due to their effectiveness at lower dosages. There is a wide selection of products that work best for different scenarios. Since they are synthetically made, there is added marketability from creating diverse flocculant species of varying charge and molecular weight. The chemical is formed by attaching monomer units through a heated polymerization reaction. Longer mixing time leads to polymers with higher molecular weights. Also, when attempting to produce a chemical with certain properties, a normal distribution is performed to check if the product has the correct properties. Those that fall outside of the bell curve are categorized by a different series number. Polyacrylamide is non-toxic; however, unpolymerized acrylamide is a neurotoxin. Acrylamide is generally polymerized into flocculants. Diallyldimethylammonium chloride (DADMAC) is another synthetic that is used which consists of polymerized monomer units. A cationic synthetic polymer would be the only charge type to flocculate algae; however one series or combination may perform superiorly.

2.1.3 Influence on other processes

Flocculation itself is a very important process. Water clarity is achieved by removing all of the suspended solids. Agglomerating the solids can have tremendous improvements on further processes. Floc structures are able to increase the ease of handling characteristics of solids. While particles may be small, flocs can be 10-100 times larger. One of the most widely used processes after flocculation is sedimentation, where the work is simply done by gravity for solid-liquid separation. If the system is stagnant enough, the cells are able to settle naturally via auto-flocculation. However, a system may never be completely motionless. Flocculant addition can increase agglomerations whose mass can overcome buoyancy. In some centrifugation units there are slotted screens to allow water to escape. Flocs can be trapped on this boundary layer to initiate solids build-up. As the bowl spins faster, more water leaves the solids.

Flocculation plays an important part in filtration. Laboratory filtration relies upon the opening pore size to be smaller than the solid that is being captured. This limits the volume that can be processed. As pores become blinded, the filtration time increases. Eventually the filter will clog completely and allow no water to pass. Having larger flocs improves filter throughput by creating void space to allow water to flow. Alum, chitosan, and other chemicals can be added in high concentrations to induce flotation (McGarry 1970). Bigger flocs have larger surface area, and in some cases density heavier than water. Air is sparged through the solution in flotation processes, such that flocs attach to bubbles and rise to the top. Non-coagulated algae cells would remain in suspension.

2.1.4 Influence on flocculation

There are also influences on flocculation itself, which are pH, flocculant series (charge/molecular weight), and dosage. The isoelectric point (ISP) is defined as the pH level at which the surface of the particle has no charge. For most algal strains, this is in an acidic range. If the pH is high, ions that are specifically present from nutrient addition can precipitate and trap turbid solids within. A major precipitate suspected is magnesium hydroxide (Vandamme et al. 2011). When there is no charge on the surface, Van der Waals forces are generally eliminated. Without Brownian motion, the particles can fall out of solution. Flocculation by chemical addition works by an alternate form of the previously described charge neutralization. Particles are attracted to an oppositely charged polymer by electro-osmosis. The diffuse double layer is the same charge as the particle; it is negative in the case of algae. The ions in the diffuse double layer are attracted to a cationic polymer, and as they move, the particle migrates. Once the activation energy is overcome, the particle will bond to an active site on the polymer. There is an optimal pH range for different chemicals. Varying pH can affect the kinetic behavior of the particles and particle-polymer reactions. The flocculant itself can influence performance. Higher charged polymers have more electro-kinetic potential to pull particles closer, which also makes for easier bonding. Polymers with higher molecular weights have more active sites, thus capturing more solids and bridging more effectively. They tend to make a “net” to capture any remaining suspended particles upon settling. Appropriate dosage range is a major factor in successful flocculation. If the dosage is too low, no flocculation will occur. Overdosing is a waste of polymer. Within that range the floc structure can vary. At the minimum, floc structures are small, allowing for tighter compaction of solids. At the maximum, floc structures are larger,

allowing for better water movement. Sometimes these larger flocs will have a tendency to float. Every factor of flocculation could have an impact on further processes.

2.1.5 Thickening

For most algae dewatering work, flocculation is the first step to further processing. It initializes solid-liquid separation. After the solids are flocculated, then they can be thickened by a variety of different ways. Ultimately there are a few thickening routes that are possible to gain specific products with acceptable moisture. The two main desired products are wet and dry biomass. Wet products could cover a broad range of 5-25 wt%. Some of the dewatering processes are capable of producing this range alone or in combination. The dry products would have to by dried using industrial dryers. The load on dryers can be reduced by using the mechanical dewatering steps. Then the focus becomes which process should be used.

Before discussing the common practices of algae dewatering, the reporting methods must first be defined. Measurements of concentrations and wt% are reported traditionally, in that the mass of the mixture is weighed, dried, and reweighed. This ensures that the sample is a true measurement, although the water content of an algae cell is 75-80 wt%. This method is useful for calculating PBR concentrations since the sample is extremely dilute. As more water is being removed, this measurement could become confusing. Thinking of the number in a new way could be more enlightening. There are two types of water in a given sample of algae, free water and bound water. If the algae contain 75% water, then the highest solids content that can be reached mechanically is 25 wt%. Only after drying, can the bound water be removed.

2.1.6 Sedimentation

In conjunction with flocculation, sedimentation is very common practice for algae dewatering. Literature shows that this is often the first thickening step. After the algae cells agglomerate, then they fall out of solution. The flocs that are formed are able to overcome buoyant forces. Larger flocs tend to fall faster than smaller flocs. This causes one of two things. Faster flocs will collide with smaller flocs and cells, potentially growing in size. Large flocs will fall and small flocs will be pushed up, causing flow patterns to circulate. Depending on the flocculant used, this could be a slow or relatively quick process. While flocs accumulate on the bottom, displayed in Figure 2.4, they will compress more water out of the slurry, 2-5 wt%. After all or a majority of the flocs have settled, the supernatant can be removed from the top and recycled to a PBR. The capture efficiency of sedimentation can be approximately 80-98%, depending on compaction provided by the flocculant and dosage.

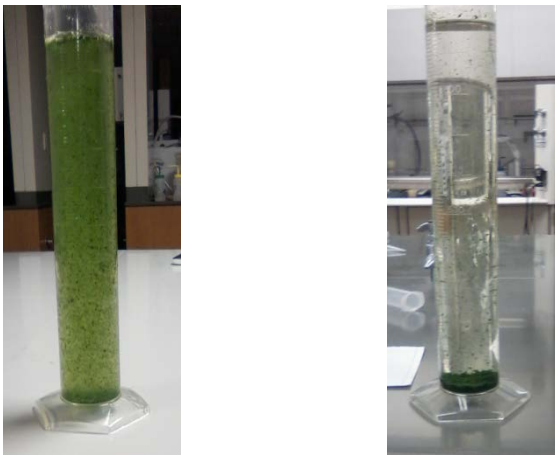

Figure 2.4: Left: Flocs are forming after cationic flocculant addition and mixing. Right: Flocs fall out of solution when static.

This example is a batch process. Industrially, there are a few designs that are able to run continuously. One common design in sludge handling is a gravity thickener that treats millions of liters of water per day, shown in Figure 2.5. Flocculant is added by Venturi into the influent pipe. The friction of the pipe and turns on the way to the thickener ensure thorough mixing. Influent flow rate is controlled so that there are no disturbances that re-suspend the flocs as it enters the thickener. Clear water should overflow into a weir and in the case of water treatment, be further cleaned and sterilized. In an algae system, the water can be sterilized and recycled as make-up water for reactors. The solids settle on the sloped bottom of the thickener. As more time passes and more solids are deposited, the solids layer compacts. A rake mechanism is utilized to slowly thrust the solids layer towards the underflow. The sludge pipe contains slurry of about 2-7 wt% depending on flocculant dosage and other operating conditions.

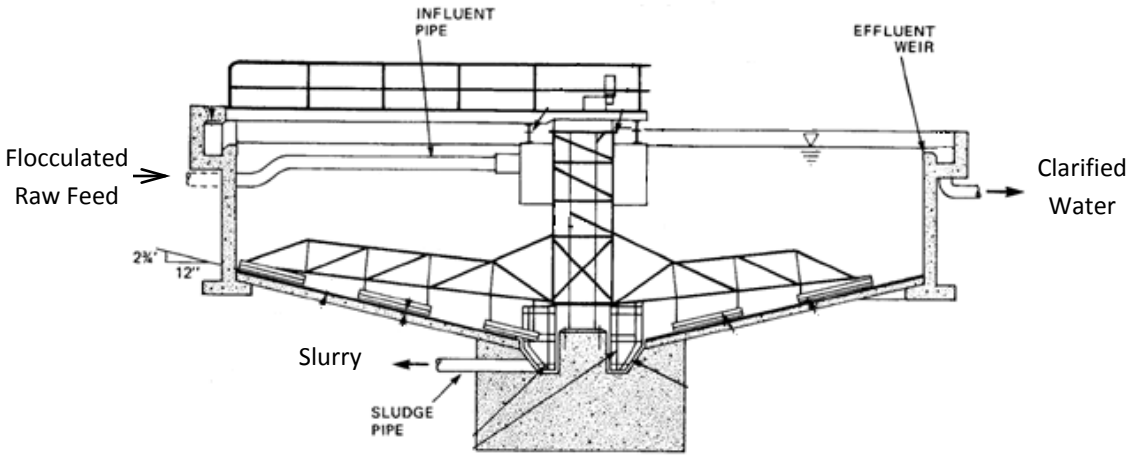

Figure 2.5: Gravity thickener side view with a single inlet and two outlets (EPA 2000a).

2.1.7 Centrifugation

Another method that is commonly practiced in algae research is centrifugation (EPA 2000b). Two masses of dissimilar density can be separated using high rotational velocities. But there are limitations to solid-liquid separation when the solid has a specific gravity near 1. High acceleration could yield other problems such as high shear. Centrifugation might rupture the cells (Divakaran and Pillai 2001). Like with any process, there are two forms of centrifugation, batch and continuous. Bowl centrifuges are used for dewatering a fixed volume of solids. When the bowl is filled, then the process must be stopped, so that the bowl can be emptied. Other versions of a bowl centrifuge in materials handling tilt the bowl so that incoming solids and the vibrations of the machine advances the cake to a collection basin. Flow-through type centrifuges rotate the incoming fluid. This rotation allows the water to separate from the algae cells. Some problems with centrifugation are the amount of energy involved in either rotating a fluid or mechanical components at great velocity. This energy would be directly associated with a higher cost of operation as well. Volume handling is also a particular problem with centrifugation. Centrifuge units can only reach a certain size before physical limitations come into play. A containment vessel must be emptied, either mechanically or manually.

Solid bowl centrifuges rated for 3,600 lph will have a 4.8 L basin and retain 1.5 L of solids. As fluid enters the spinning bowl, heavy particles and/or fluids locate to the walls of the bowl. Clarified liquid will reach the top and be flung out into the larger bowl. This operation would require the bowl to be cleaned routinely. The machine must be stopped and the bowl ran manually emptied. Disc stack centrifuges use plate-type technology to help separate solids (Figure 2.6). Slurry flows through openings in angled discs while traveling up the bowl. High rotational velocity causes the particles to reverse their motion between the discs, while the water continues its path upwards. Solids accumulate in a bowl with a small discharge opening. These openings are generally in a location away from the clarified product. Openings are closed via a plate or other design and a piston lowers allows the openings to discharge.

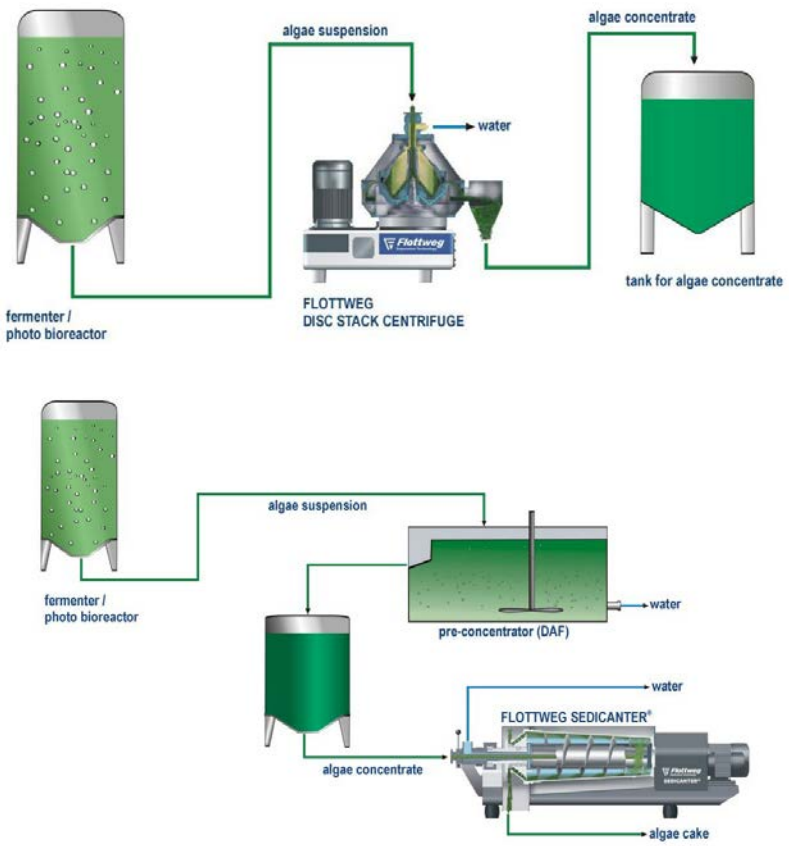

Figure 2.6: A diagram showing typical thickening process with a disk stack (top) and a decanter (bottom) centrifuge (Flottweg 2016).

A decanter centrifuge not only exploits gravitational forces due to high rotational velocity, but also pressure forces that squeeze the solids (Figure 2.6). The body of the decanter is tapered, while the auger that transfers material forward is straight. Reducing volume is what drives water from the solids. Slurry is carried to the middle of the auger. Solids will get trapped by the motion of the auger and transferred toward the taper. Clarified water will exit towards the rear of the decanter near the inlet. There could be limitations of solids compaction and throughput with centrifugation systems.

2.1.8 Filtration

There are a wide variety of filtration processes of filtration, many originating from mineral processing applications. There are different approaches for solids handling. In a laboratory setting, a suspension is poured through filter paper. This is typically performed with untreated biomass from a PBR to attain the reactor concentration. This action is more like screening or seiving in that the cells cannot pass through the undersized pores. Even under vacuum, the process could take a lot of time, especially when there is a large volume to be processed. Cake formation is a similar function that is shared for large scale separation. A filter medium is used to establish cake formation, while the cake actually filters the influent (Figure 2.7). Feed solids are deposited onto the medium, increasing the cake thickness. There is a point when no more solids can pass through openings and only water can escape. Flocculation aids in cake formation since

the flocs can be larger than the particles tenfold. This also allows for larger orifices in the medium and higher rated air velocities, a specification for filtrate throughput.

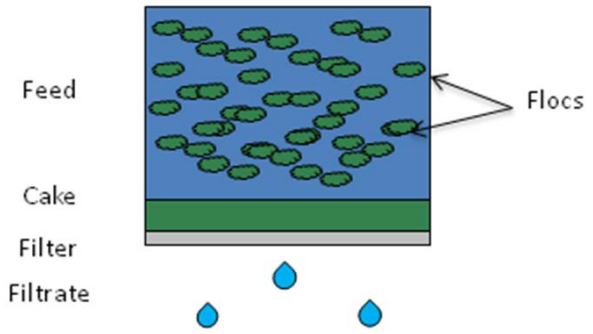

Figure 2.7: Cake filtration diagram showing flocs in suspension that will build up more cake.

There are many different forms of and types of equipment used in filtration. The equipment can be categorized by belt, plate, and drum. The style of the category can vary from gravity, pressurized, and vacuum. Each set-up may be better suited for different materials. The smaller size of some algae strains causes problems with filtration. Even when flocced, the cells clog pores in the filter medium. With added pressure, the cells will break through the filter medium; so more investigation should be conducted on filtration with alum and chitosan treated algae due to their lower molecular weight providing more liklihood of breaching the filter (Sim et al. 1988). Flocculant selection and dosage could have a major impact on the performance of filtration. As with many other dewatering techniques, flocculation is used to accelerate filtration processes.

Belts

Belt presses have a significant advantage in that they don't consume large amounts of energy. A small electric motor is generally used to drive the belt, making it a continuous process. A belt press will incorporate a gravity section to drain a portion of free water. Plows might also be integrated in the gravity section to open drainage zones in the cake. The next portion of a belt filter may either be pressurized or vacuum assisted. In the case of most pressure belt filters, there is another belt filter that runs parallel to the operating belt (Figure 2.8). The cake is sandwiced between two layers of filter medium. As the belt makes a turn around a roller, the cake is squeezed. This added pressure forces water out of the cake. Pliable substances are able to move through the pores of the belt or the edges where the two belts meet. This occurs if the solids are not rigid enough to withstand high pressure. Most algae strains are mostly comprised of water and their cell walls conform to pass through openings. Flocculation may not solve this problem. Bridging mechanisms are typically hydrogen or other weak bonds. Flocs will not be able to withstand extreme pressure.

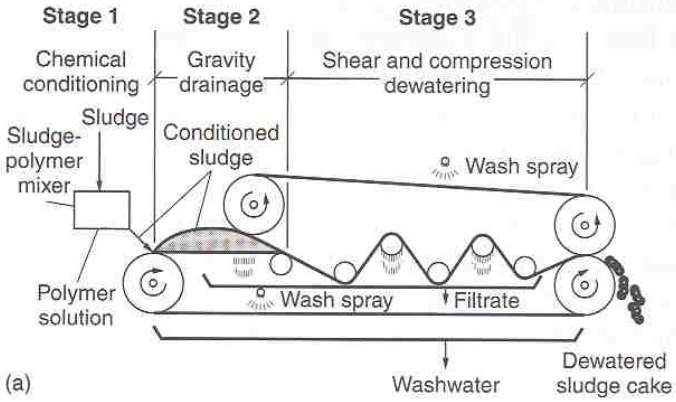

Figure 2.8: Pressure belt filter press diagram shows a pretreatment, gravity, and pressure stage (Stensel et al. 2013).

In vacuum belt filtration, the mechanics are much the same (Figure 2.9). Water is pulled instead of pushed through the cake. After a gravity drainage, a portion of the belt would have a vacuum pan to assist in moving water. Sealing for the vacuum section is stationary and more controllable. The cake assists in providing a seal to establish a pressure drop through the belt. Solids capture should be more effective for algal biomass since the cake is not physically disturbed as with pressure belts.

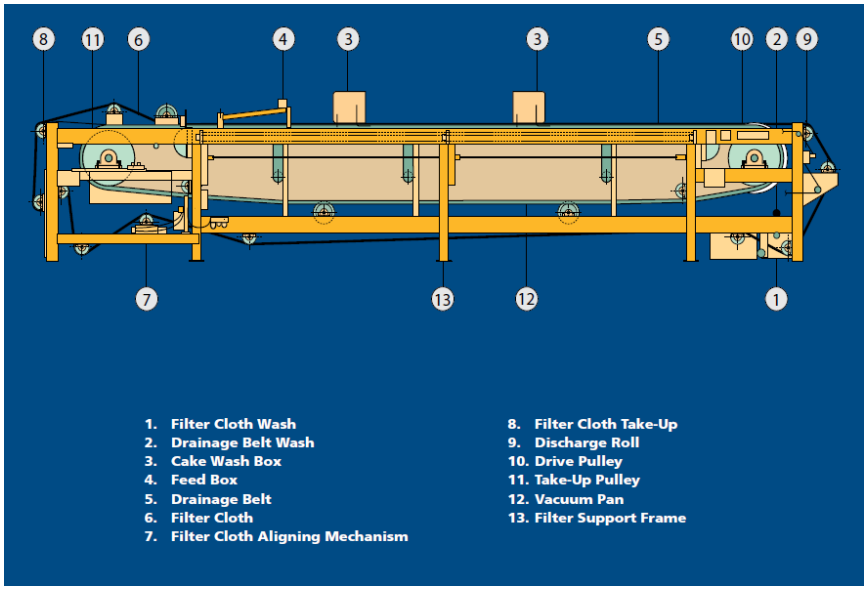

Figure 2.9: Vacuum belt filter diagram (FLSmidth 2016).

Plates

Plate filtration uses pump pressure to force the slurry through a filter medium (Figure 2.10). There are plates that stack together. The only path for water to escape is through the membranes of every plate. This type of filtration allows for extremely high pressure.

The cake is trapped between individual plates and can be removed by separating the plates. Hydraulic cylinders stack the plates and create a seal. They can also squeeze residual moisture after enough solids are deposited. The semi-batch continuous process must routinely, and automatically with newer models, stop the incoming feed slurry in order to discharge solids (EPA 2000c).

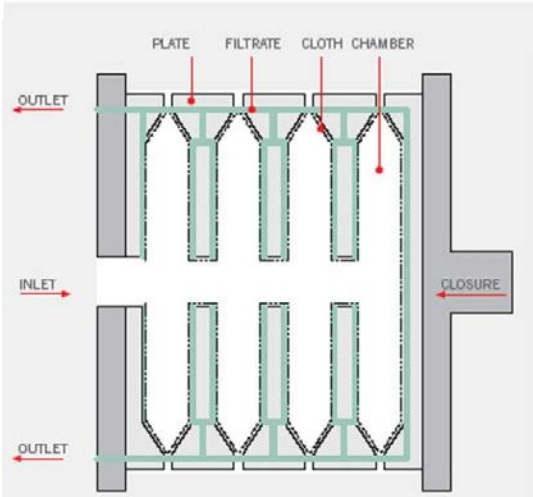

Figure 2.10: Schematic of a plate filter press (Lenntech 2016).

Drums

Drum filtration equipment is very efficient and has a low aerial footprint. The floor space becomes less occupied by converting a flat filter surface to cylindrical. For vacuum applications the drum rotates through a slurry mix normally occupying 1/3 of the drum's surface area. One inadequacy of the system is the area between a wicking blade and the slurry level, this is the unused filter area. A filter medium mix, typically diatomaceous earth, is initially run through the vat to create the filter. Pressure drums operate in reverse where the slurry is fed inside the drum and the cake thickens as it rotates. The cake is usually discharged by back flowing air or filtrate. Both processes require large energy inputs. A detailed diagram of a vacuum drum filter designed by Komline-Sanderson is presented in Figure 2.11.

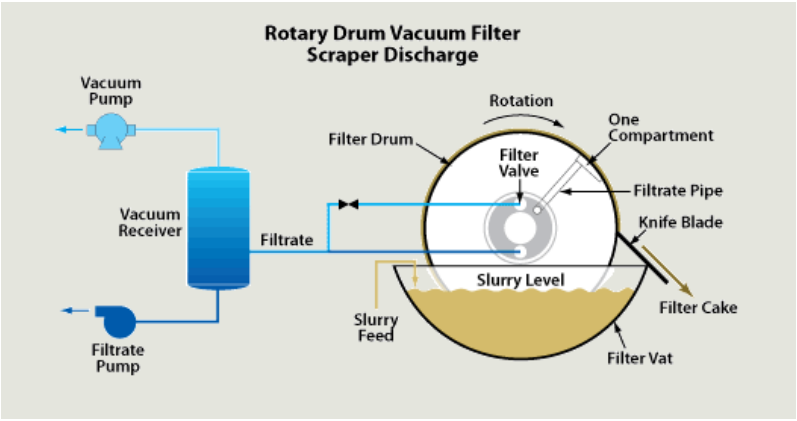

Figure 2.11: Schematic of a rotary vacuum drum filter (Komline-Sanderson 2016).

2.1.9 Drying

Reducing the load of drying is pertinent to reducing the energy usage for dry route algal biomass. Solids with higher moisture content associates to higher carbon emissions, whether through on-site heat generation or electric consumption. Since the dryer cannot be avoided, via the fixed cellular water, other areas have to be optimized to minimize the amount of carbon emissions. Removal of free water mechanically reduces additional thermal load.

Some literature suggests spray dryers should be used to attain a dehydrated algal product (Shelef et al. 1984). Cyclone spray dryers are commonly used in dried powders, including spray dried milk. Inlet fluid is atomized allowing for rapid heat transfer of evaporation gases. A cyclone separates the dried solids from the moist drying air. There are large energy demands for atomizing the feed, heating air, and moving the fluids (mixtures) at great velocity. While the process is swift microscopically, it takes a long time to process large volumes. Scaling of equipment to handle the potential demand of dry biomass could be a hindrance. But, handling raw PBR harvest and converting it to dry biomass with one piece of equipment is very beneficial.

Cross flow dryers are used most commonly, not only in the algae field, but also in many other applications. Drying ovens of many sizes are regularly used in laboratories. Conveyor ovens could serve as a continuous operation solution. For either of these dryers, less moisture translates to faster process times. Another factor is size and shape of the samples. As more free water is removed, the physical properties and handling characteristics change. A volume of biomass inherits adhesive properties during thickening most likely due to excretion of polysaccharides. It becomes almost a semi-solid, paste, at approximately 7 wt%. The maximum solids content for most algae strains is around 25 wt%, which behaves like a wet cake. Thinner cakes or cakes that are broken into pieces will dry much faster by mechanics of conduction and convection. This drying process would be the standard convention of drying; mainly due to the reasonable energy consumption and biomass throughput rate.

Solar dryers could be a cheaper alternative, as long as the available solar energy is enough to provide the appropriate amount of drying. Most designs would incorporate polycarbonate paneling or similar materials used in greenhouses. The elevated temperature could dry algal biomass completely without any energy contribution. Solar dryers would be most effective in hotter months. In winter months, the unit might require additional heat possibly through natural gas heaters. Solar panels could be coupled with electric heaters for a sustainability approach.

2.1.10 Flotation

Some culturing photobioreactors have air or CO_2 streams to mix the algae. Froth flotation, also called dissolved air flotation (DAF), is used to float small particles up from the surface. Usually it is coupled with other dewatering techniques such as sedimentation and especially flocculation. This practice is used to separate particles by size. Smaller particles are able to be lifted by buoyant air bubbles. Bubbles adhere to the particle surfaces similarly to carbonation on the side of a glass. Heavy particles will sink to the bottom of the tank. The low concentration of cells makes this process intriguing in the algae field. Surfactants and other chemicals can be added to absorb materials and

maintain a froth on the liquid surface (Chen et al. 1998). Bubble size and chemical addition play a crucial part in the effectiveness of flotation.

2.1.11 Electro-coagulation

Since the algae cells are negatively charged, passing them by positively charged plate can collect them at an anode (Figure 2.12). The concept is very similar to electrostatic precipitators in combustion gas, however the fluid is liquid. In combustion gas, smaller ash particles are easily captured because of high density and high charge and low particle diameter. The same occurs in algae suspensions. Most algae cells are roughly 5 µm and have a sufficient charge. Therefore they are able to migrate by electrophoresis and overcome smaller inertial and drag forces. By electrolytic oxidation, Iron or aluminum ions, Fe^{2+}, Fe^{3+}, and Al^{3+}, are shunted from the anode and flocculate the negatively charged algae cells (Vandamme et al. 2011). Hydroxides may also be formed, and the flocs are able to settle. Since no chemicals are added, accumulation of heavy metals or residual compounds is less likely. However, metal ions are being released by large electrical requirements.

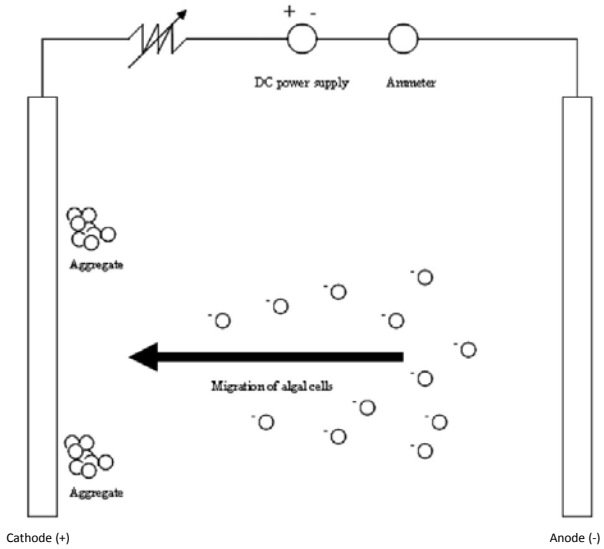

Figure 2.12: Electro-coagulation will draw particles towards an oppositely charged electrode (Udaman et al. 2010).

2.2 Existing Algae System

Of the many variations of photobioreactors, whether they are open or closed systems, there are numerous strategies for harvesting algal biomass. Motivation for fuel replacement and carbon credits require large quantities of algae. Even if the biomass production is the main goal, cells have to be removed to maintain a stable culture density. As PBRs inflate in size and quantity, a responsible harvesting strategy is essential to handle all of the accumulated biomass. An algae harvesting strategy must be set in place to collect the biomass while limiting energy input or emissions output, regardless the intentions of an algae system. There is insufficient evidence of successful algae dewatering systems. This chapter will introduce an algae biomass management strategy to compliment closed PBRs currently in use at the University of Kentucky.

Harvesting biomass is necessary to maintain algae density (0.4-1.0 g/L) and allows for the recycled water to be sterilized, reducing contaminant population such as rotifers. The harvesting system includes flocculation, sedimentation, and filtration (Figure 2.13*)* Thickened slurry (20-50 g/L) from the process could be sent to anaerobic digestion or other processes such as wet lipid extraction to ultimately produce biodiesel. Slurry could also be fed on a belt filter to further remove water, producing an algae paste (80-120 g/L). The algae concentration of the paste is approximate and based on the filtration by gravity alone. A vacuum could be applied to remove more free water. In this work, research on sedimentation and filtration is necessary to confirm these processes could be executed on larger and possibly commercial scales using industrial equipment; gravity thickeners and filtration units.

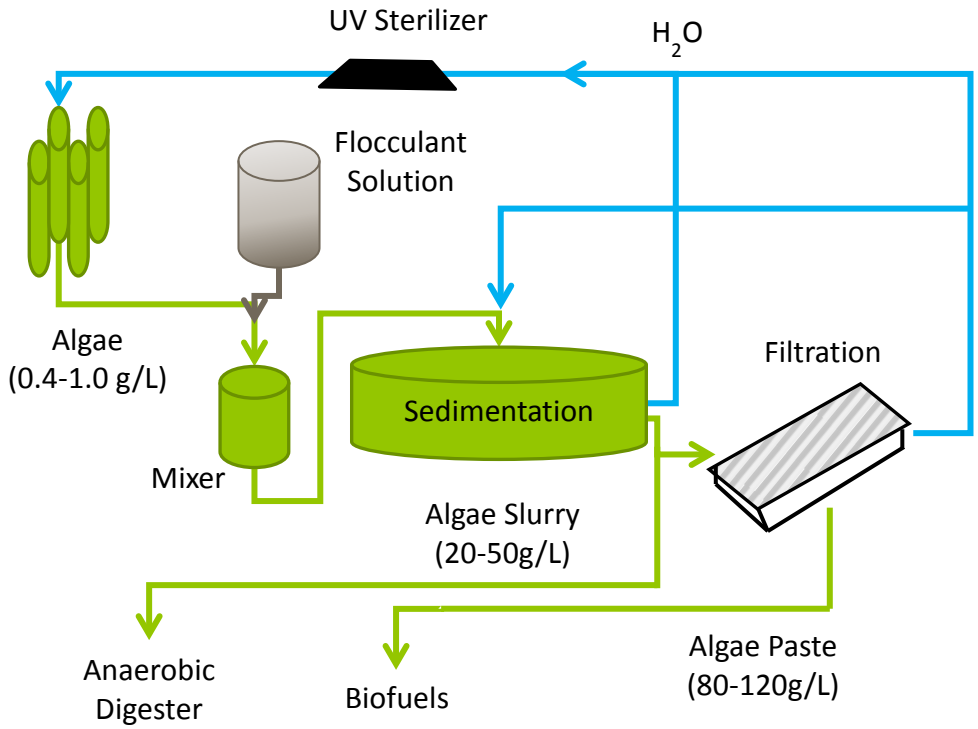

Figure 2.13: Algae harvest process diagram showing sedimentation and filtration.

An "Algae Supply Chain" must be sustained in order to ensure that there is always a healthy source of fresh algae. Cultures start as frozen samples from the University of Texas at Austin that are applied from agar plates to flasks as start-up culture. This work is reliably performed in the laboratories of UK's Biosystems and Agricultural Engineering (BAE). As the cells begin to multiply, they must be moved to larger reactors. Nearly 2 L of flask-grown algae can inoculate the airlift reactors. Algae culture grown for 2 or more weeks can be added to a larger reactor. From experience, a successful initial concentration is greater than 0.05 g/L. This process could repeat infinitely, but there is a point where the reactor size becomes unmanageable and harvesting can no longer be performed effortlessly. The supply chain is simplified in Figure 2.14. Typically, flasks are transferred to airlift reactors (8 L each), then to the 500 L Varicon (also referred to as the biofence), then to the 2,500 L PBR (referred to as the serpentine), and then harvested by first moving the 500 L harvest tank.

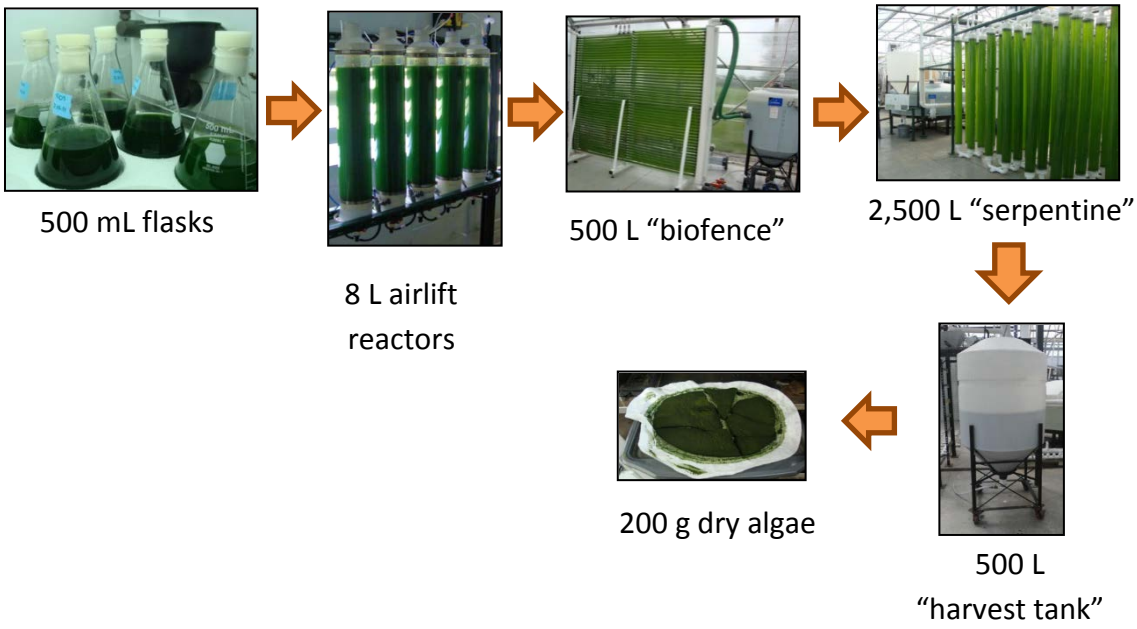

Figure 2.14: Algae supply chain. Values are rounded to whole numbers.

The supply chain also has other reactors at both University of Kentucky collaborating partners. Multiple reactors aids in convenience to accommodate algal biomass. Volumes can be moved where they are needed. Other reactor types and sizes can be seen in Figure 2.15. This is a Trailer reactor designed to be mobile and includes instrumentation. All large scale reactors, the Serpentine, Trailer and Varicon have sensors for pH, dissolved oxygen, and dissolved carbon dioxide. Automation dictates whenever the pH drops below 6.6 that compressed CO_2 gas is fed at 1.0 scfh until the pH reaches 6.6. The gas is 98% pure CO_2, which is metered continuously at approximately 0.3 lpm for each airlift reactor. Each reactor has been harvested using the aforementioned harvest strategy in section 3.1.

Figure 2.15: Trailer reactor located outdoors at CAER.

A separate system, seen in Figure 2.16, has been initiated at BAE to culture algae in a controlled environment. In these laboratories, the cultures can be grown in similar conditions. Both facilities are able to sustain their own Algae Supply Chains from flasks to Airlifts to reactors. BAE culturing systems share a commonality of CO_2 addition, lighting, and cleanliness. Carbon dioxide is metered continuously for all systems at BAE. Each scale has optimal lighting conditions with cool and warm fluorescent bulbs and also photosynthetic LED. CAER utilizes natural sunlight in effort to culture algae under natural elements. Cleanliness is an overlooked asset. The Trailer is the largest reactor at BAE and has been designed to be easily disassembled. Airlifts have also been designed with this asset. Speedy cleaning and strict laboratory practices have led to successful culturing at BAE. The Trailer and Airlift reactors have sustained prolonged growth with dilution and nutrient addition through make-up water.

Figure 2.16: Trailer reactor located indoors at BAE; 115 L.

An algae PBR has been sited at Duke Energy's East Bend power station as seen in Figure 2.17. Flue gas from the coal-fired power plant is fed to the reactor. It is the largest reactor built by the University of Kentucky and its collaborators. Construction began in the summer of 2012. The reactor encompasses instrumentation and automation used on other CAER reactors. Test operation began in fall and an algae culture was grown during the winter. Expansions were made in summer of 2013 during operation. Frequent harvesting supports algae health. Therefore an adequate, efficient dewatering strategy is demanded for large harvest volumes.

Figure 2.17: Duke Energy, East Bend Station pilot reactor; 20,000 L.

2.2.1 Preliminary harvesting techniques

Necessity of a reliable, swift dewatering strategy becomes pertinent as the size of reactors increase. Over a few years in the major project's existence, a batch-process dewatering strategy was developed through proof-of-concept testing. The steps for harvesting are seen in Figure 2.18. Cationic flocculant is mixed in water to suspend and allow for the long chain polymers to unfold. A volume of algae is pulled from a PBR to a settling tank. The flocculant is added to the harvested algae and stirred for 5 minutes to ensure adequate mixing, dosage can vary. After the biomass has settled, the supernatant can be decanted and recycled through an Ultraviolet (UV) Sterilizer or discarded as waste. The UV sterilizer from Emperor Aquatics is exploited to kill any bacteria or other unwanted organisms before recycling the water. Supernatant is pumped through slowly to ensure enough light exposure for a 99% kill rate of all organisms before being reintroduced to the PBR. Underflow slurry can be poured onto a filter. It also was designed as a solar dryer. Slurry is poured at the gravity stage of the belt and allowed time to drain. The belt can be advanced to continue draining and drying if there is more slurry to be added. This operation may not be continuous; however it is sufficient to handle the volume of biomass from the East Bend PBR.

Figure 2.18: Harvesting process. Top-Left: Suspending flocculant in a solution. Top-Right: The flocculant is mixed in a harvest tank. Bottom-Left: Algal slurry is applied to in-house belt filter. Bottom-Right: Make-up supernatant water with UV Sterilizer.

Algae slurry from the thickener can be loaded into an anaerobic digestion for methane production. Biomass can be thickened further by gravity draining through a filter medium. Figure 2.19 displays some of the earlier forms of gravity filtration performed on large harvest samples, 1000 L. This process generally would take 4 hours to complete before the biomass was placed in a drying oven. The belt thickener works consistently with the expectations gained by this study.

Figure 2.19: Left: Algae slurry after decantation; ~2 wt% Right: Algae paste after gravity drainage; 13 wt%.

This harvesting strategy was also performed at a medium scale. The harvests at BAE are flocculated and filtered with gravity and vacuum filtration. Regular bi-weekly harvests of 110 L are taken from the Trailer reactor. Figure 2.20 shows flocculant being added to a smaller harvest tank and allowed to settle. The supernatant can be decanted and a slurry will need further processing. Airlift reactors can be flocculated in a similar manner.

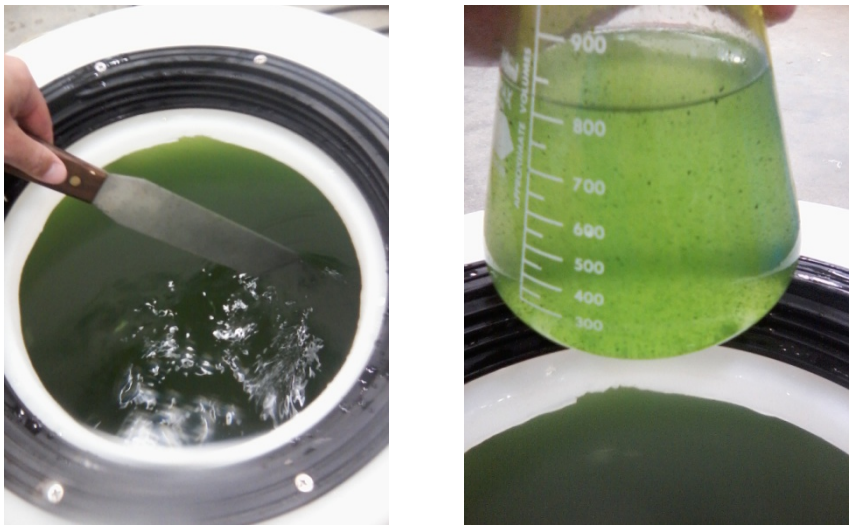

Figure 2.20: Flocculant being mixed into 110 L of algae. Flocs can immediately be seen.

The slurry obtained after sedimentation can be filtered to shorten drying time. The slurry is either placed on a filter in a drain pan or a Buchner funnel. Either is able to drain with gravity for convenience, but the funnel can be attached to vacuum. The set-up can be seen in Figure 2.21. Vacuum filtration takes time due to the large volume needed to be processed on a small diameter filter.

Figure 2.21: A vacuum pump attached to a filter flask with a Buchner funnel. House vacuum can also be attached.

There is difficulty in creating a sufficient seal with a filter medium placed in the funnel. Cakes with high solids content similar to Figure 2.22 are produced. Approximately 2.5 gallons of slurry can be processed with this small, tedious arrangement. Similar cakes are found when allowing biomass to gravity drain overnight and because of ambient evaporation.

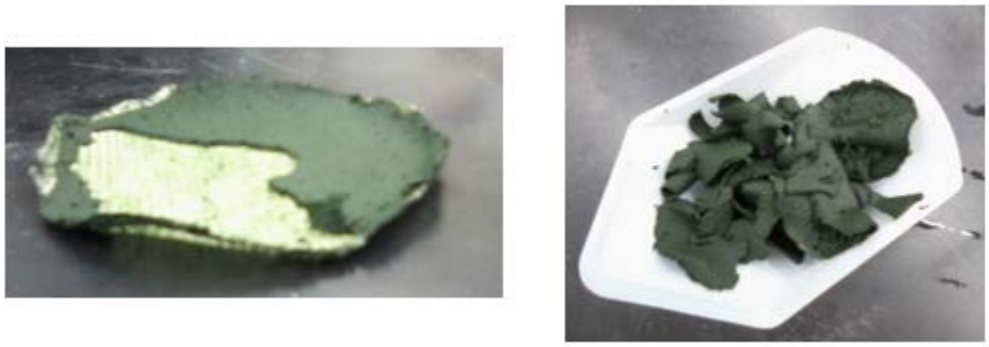

Figure 2.22: Cake solids produced from vacuum filtration; 20-25 wt%.

Weekly harvesting of the East Bend reactor began in June 2013. Approximately 3,780 L of the system volume is collected in the harvest tank in Figure 2.23. A side port was installed for decantation and mixing. The port can be opened and drained into a blue drum and ran in a recycle loop via submersible pump to mix. An appropriate, pre-mixed dosage of flocculant is added to the blue drum and allowed to mix for approximately 10 minutes. Flocs are allowed to settle until the next time of convenience, usually the next

day. The supernatant is decanted by draining through the port near the top of the cone. Supernatant can be pumped by the submersible pump in the drum through a large UV sterilizer and back into the main process tank. Inside of the harvest tank, the port extends down towards the bottom of the cone. Liquid can siphon down to approximately 100 L. Since there is no certainty of the remaining supernatant, this slurry can be placed in a secondary thickener. Only a few buckets are needed to bring biomass back from the pilot site where it can be further processed on the gravity belt thickener at the University.

Figure 2.23: East Bend Reactor. Left: Harvest tank, 6,000 L. Right: Process tank, 15,000 L.

CHAPTER 3 EVALUATION OF FLOCCULATION AND SEDIMENTATION FOR DEWATERING OF ALGAL BIOMASS

Nicholas Rhea, Jack Groppo, and Czarena Crofcheck

3.1 Summary

As algae can be used as a feedstock for agricultural fertilizers, livestock/poultry feeds, anaerobic digestion, and biofuel production. Regardless of the end product, water removal is necessary and difficult to do cost effectively. For each product the requirements for moisture content (or solids content) vary, such that a desirable water removal strategy would need to be adaptable to varying levels of water removal. Flocculation, with sedimentation and drying was evaluated as a possible strategy for algae dewatering. Anionic and nonionic flocculants are known to be ineffective at flocculating algal culture, which was confirmed for this case by electro-osmotic flow testing of the algae and jar tests with three flocculant charge types. Electrophoretic mobility of the algae indicated that it has a negative charge and no flocs were present in the jars. The effectiveness of the cationic flocculant was determined by measuring settling rates, supernatant turbidity, and filtration rates. Sedimentation rates of *Scenedesmus actus* were measured with varying dosages (0-25 ppm) of a synthetic cationic polymeric flocculant. The results of this study should assist in predicting the time it takes to thicken algae from a culture concentration range of 0.4-1.0 g/L to a product at a concentration range of 15-50 g/L.

KEYWORDS: algae, flocculation, filtration, dewatering, thickening, sedimentation

3.2 Introduction

Many algae species have been used as a food source, nutritional supplement, food additive, pharmaceutical, cosmetic, animal feed, and have potential as biofuel/energy (Pulz and Gross 2004). Kelp, a brown algae, is a prominent ingredient in Asian cuisine. Some strains of *Spirulina* and *Chlorella* are marketed as health foods (Noue and Pauw 1988). Compounds such as β-carotene can be extracted for vitamins. Much interest in algae is due to what they contain. Some strains of microalgae may contain elevated concentrations of polysaccharides, proteins, or lipids. They may be processed for different applications, depending on which organic compounds are present.

The utilization of algae as a feedstock for alternative fuel source and also as mitigation for CO_2 has the potential to address many energy and environmental problems. One problem is harvesting and retrieving algal biomass. In particular, dewatering processes are a major hindrance in employing algae systems. For large amounts of CO_2 mitigation, large amounts of algae must be grown. That algal biomass will need to be harvested consistently to maintain an operating system. Algae is said to be harvested whenever the dilute suspension of 0.02-0.06% TSS (total suspended solids) is collected and then conditioned to 5-25% TSS or higher (Shelef et al. 1984). Culturing systems are typically a dilute suspension of microscopic cyanobacteria, formally referred to as blue-green algae. Processes downstream demand only the algal biomass and not the huge volume of water that follows.

Since there is such a large burden to remove water from algal biomass, one technology suggested is to use flocculation to remove algae from suspension. This process actually makes the cells susceptible to other handling techniques. Using some secondary thickening process is required for higher solids. Other thickening equipment under speculation is centrifugation, pressure filtration, vacuum filtration, flotation, and many more. Thickening means that the viscosity of a substance is increased by reduction, or some means of water/liquid removal. Dewatering is the removal of water from solids in a mixture by these and other types of wet classification.

Harvesting biomass is necessary to maintain the algae culture density (0.4-1.0 g/L) for most bioreactors and allows for the recycled water to be sterilized, thereby reducing contamination. The harvesting system includes flocculation, sedimentation, and filtration (Figure 3.1). These unit operations were selected because they are standard thickening processes that are used in commercial applications, such as wastewater treatment and mineral processing (EPA 1987). Thickened slurry (20-50 g/L) from the process enables direct utilization of algae for methane production via anaerobic digestion. Further dewatering by gravity filtration produces an algae paste (80-120 g/L) amenable to wet lipid extraction for biodiesel production. Other potential utilization options, such as biodiesel production via dry lipid extraction or bioplastic production, require moisture reduction to levels that can only be achieved by thermal drying (i.e., <10% moisture). While thickening and filtration cannot achieve these moisture levels, they are essential steps for removing a substantial amount of water prior to applying thermal processes.

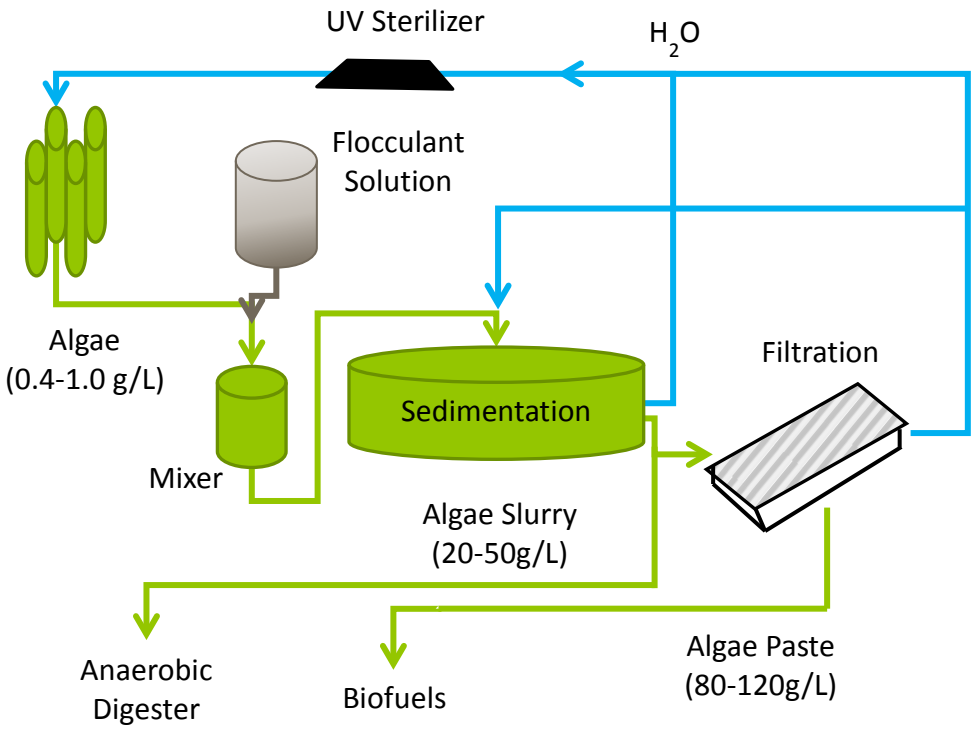

Figure 3.1 Algae harvest process diagram showing sedimentation and filtration.

The goal of this work was to evaluate the processing conditions required for thickening harvested algal biomass to the consistency requirements for further utilization, while

simultaneously providing acceptable clarified water quality to enable recycling of soluble nutrients as well as minimizing water consumption. Determination of process conditions required for effective sedimentation performance will confirm the plausibility of using these standard industrial techniques to dewater large scale algal biomass. The specific objectives include selection of the appropriate flocculants and evaluation of their performance on sedimentation/thickening process. While thickened biomass would be suitable for further dewatering via filtration and/or centrifugation, the subject study focused only on sedimentation and thickening; Results of filtration performance have been completed and will be addressed in a subsequent study.

The microalgae used in this study (*Scenedesmus actus*) was cultivated in airlift photobioreactors (PBRs) utilizing sparged CO_2. Individual cells of the organism are approximately 5 µm in size, contain 80% intercellular water and have a density of ˜1.0 g/cm^3. Dry mass concentration of the organism in the PBR is dependent on growth conditions and periodic harvesting is necessary to maintain a culture density <0.3 g/L (dry weight) to minimize photoinhibition. Harvesting consists of removing a significant portion of the PBR system volume (typically 80%), separating the algae cells from the process water via sedimentation, and recycling clarified water and soluble nutrients back to the PBR to dilute the remaining culture for another growth cycle. Given the small size and low density of the algae cells, natural sedimentation is a very slow process, thus increasing the sedimentation rate was the focus of this investigation.

Various chemicals have been evaluated to increase algae sedimentation, including alum (Golueke and Oswald 1965, McGarry 1970, Moraine et al. 1980), ferric sulfate (Bare et a1. 1975, Moraine et a1. 1980), lime, and magnesium hydroxide (Folkman and Wachs 1973, Friedman et al. 1977) as well as chitosan (Nigam et al. 1980). While these materials can induce coagulation; the large dosages required, the need for pH control, and the introduction of soluble ions into the recycled water preclude this approach for continuous large scale application. Because of these limitations, polymeric flocculants were selected for evaluation as sedimentation aids. Polymeric flocculants are widely used in a number of industrial water treating applications, such as municipal waste and mineral processing water treatment. A detailed review of early investigations using polymeric flocculants for algae treatment is provided by Shelef et al. (1984).

Polymeric flocculant charge, charge density, and molecular weight are important considerations for selecting the appropriate flocculant to induce settling in any suspension. Stable particulate suspensions are characterized by a high zeta potential, indicating that electrostatic repulsive forces within the electrical double layer surrounding each particle limit particle migration within proximity close enough for shorter range attractive forces to operate, thus the highly charged particles remain in suspension. The addition of large polymeric flocculant molecules of opposite charge provide charged active sites for oppositely charged particles to adsorb. If the flocculant molecule is sufficiently large to provide numerous adsorption sites, floc formation occurs. The electrostatic attractive forces of oppositely charged particulates and flocculant molecules in this type of system is considered the primary mechanism for adsorption. Active sites on long chain polymers can induce further aggregation of flocs by attachment via bridging mechanics (Somasundaran 1980).

With the selection of the appropriate polymeric flocculant, a dilute suspension of algae cells can be induced to form flocs of sufficient size to promote effective settling despite the small size and low density of algae cells. Primary advantages of using polymeric flocculants compared to inorganic additives are a significantly lower dosage (5-10 ppm versus 100-750 ppm), elimination of the need for pH manipulation, and avoidance of introducing excessive inorganic species into recycled water that can inhibit algal growth.

3.3 Materials and Methods

3.3.1 Algae cultivation

Microalgae was cultivated in 4' tall x 5" diameter airlift reactors using tap water sterilized with a UV filter and urea media and cultivation procedures described by Crofcheck et al. (2012). The urea media included 0.138 g/L of urea, 0.14 g/L of TS Phosphate, 0.068 g/L Potash, and 0.026 g/L Sprint 330 EDTA. The culture was grown outdoors under natural light and continually sparged with a mixture of compressed CO_2 (12% v/v) and air to simulate coal combustion flue gas. The culture of *Scenedesmus acutus* algae (UTEX B72) was grown autotrophically and periodically harvested when appropriate culture density was achieved, typically >0.4 g/L dry mass concentration. The remaining culture make-up water was diluted with water containing additional nutrients to avoid nutrient depletion.

3.3.2 Zeta potential

Electrokinetic properties of algae cells were characterized by determination of the zeta potential using a Zeta-Meter GT-2 Electrophoresis cell. A 1 mL sample of algae suspension was collected from the 8 L air lift reactors and diluted with 50 mL of a 10^{-4} molar solution of NaCl prepared in distilled deionized water to maintain constant ionic strength. The sample was mixed using a magnetic stirrer and pH adjustments were made using dilute 1 M HCL or NaOH. Once the pH stabilized, the sample was transferred into the electrophoresis cell. DC voltage was applied to electrodes at opposite ends of the cell. As algae cells migrated to electrodes of opposite charge, the time required to move between fixed distances on a calibrated scale was recorded. Measurements were taken for a minimum of 10 particles at each pH value; the average and standard deviation of zeta potential for each pH measurement was recorded. After measurement, the cell was thoroughly cleaned and rinsed prior to the next measurement.

3.3.3 Flocculant selection

Three types of polymeric flocculants; anionic, nonionic, and cationic; were initially screened to select the appropriate additive to induce flocculation. The flocculants selected for this initial screening were dry polyacrylamide based products with 4M to 6M molecular weight. The procedure used for screening was to prepare a 0.1% w/w solution of each candidate flocculant by adding 0.1 g to 100.0 g of water in a magnetic stirrer. A small initial dosage (1 to 5 ppm) of flocculant was added to a fixed volume (1.0 L) of algae suspension in a graduated cylinder. The flocculant was mixed with the algae using a perforated disc attached to a plunging rod by plunging the rod through the entire cylinder depth three times to ensure thorough low-shear mixing. In this manner, each sample was mixed consistently. The suspension was observed for 15 minutes to visually assess the extent of flocculation. If no visual evidence of flocculation was observed, the

procedure was repeated with higher flocculant dosages in intervals of 5 ppm up to 20 ppm. Based upon the results from (McGarry 1970), it was determined that cationic flocculants were the most appropriate for flocculating algae cells.

A series of cationic polyacrylamide flocculants (Table 3.1) were selected for further evaluation and provided by Zinkan, Inc. The flocculants were selected to provide a range of molecular weights with similar charge density. An additional product was included because of its very high charge density, namely Zinkan 6702, a medium molecular weight diallyl dimethyl ammonium chloride (DADMAC) flocculant.

Table 3.1: Cationic flocculants used for sedimentation experiments.

Zinkan Flocculants (synthetic polymers)	Form	Charge	Mol. Wt.
6702 DADMAC	Dry powder	100%	Medium
540 Polyacrylamide	Liquid solution	50%	High
440 Polyacrylamide	Liquid solution	40%	Low
670H Polyacrylamide	Dry powder	40-60%	Medium

3.3.4 Settling tests

Since the harvested algae suspension was very dilute (typically <0.5 g/L dry mass), no well-defined interface of settling solids was evident at any point during settling time period. Rather, flocculated solids were dispersed in the suspension and settled with time, accumulating at the base of the settling cylinder. For this reason, it was decided to measure settling performance using Imhoff settling cones, 1.0 L tapered cones with graduations to enable measurement of settled solids volume as a function of time (Figure 3.2).

Figure 3.2: Imhoff settling cones used for triplicate sedimentation testing displaying a liquid supernatant layer above and slurry layer containing solids below.

The settling test procedure consisted of combining 1.0 L volume of algae suspension and an appropriate dosage of flocculant into a 1.0 L beaker, and stirring for 1 minute on a Super-Nuova™ four position magnetic stirrer at 600 rpm to ensure consistent low-shear mixing conditions. The flocculated volumes were then immediately transferred to 1.0 L Imhoff settling cone, a timer was started and at appropriate time intervals, the volume of the compacted solids was recorded and converted to mass based on the algal dry mass density. Settling tests were completed in triplicate and results reported as an average. Sedimentation experiments were conducted varying flocculant dosage and algae culture density. The flocculant dosages tested were 2.5, 5, 10, 20, and 30 ppm while the culture density range evaluated was 0.25, 0.5, 0.75 and 1.0 g/L. The culture density range was selected based upon the anticipated productivity that would be expected from a large scale algae cultivation system. To achieve the range of algae culture densities required for testing, airlift reactors were cultivated until the highest desired culture density was achieved of 1.0 g/L. A sufficient quantity of culture was collected to complete testing, which was performed within 12 hours of sample collection. In order to complete the experiment on algae under the same growing conditions, it was determined most effective to dilute the harvest sample to procure lower culture densities. The BAE trailer reactor had sufficient lighting to obtain 1.0 g/L and large enough for the 60 L used during testing and spare for adjustments. Dry mass determinations were made using representative 25 ml samples of the algae culture. The culture sample was vacuum filtered using Whatman 0.45µm filter media, then dried at 100°C for 24 hours. The dried samples were then placed in a desiccator for 1 hour before weighing.

To quantify water clarity, a 30 mL sample of supernatant was collected for turbidity measurement at the end of the 30 minute settling time. The turbidity sample was withdrawn by pipette from the center of the Imhoff settling cone at a depth of 16 cm. Turbidity was measured with a LaMotte Turbidimeter, repeating five times. Between measurements the sample vial was shaken to redistribute any settled solids. Turbidity measurements are reported as an average of the five measurements.

3.4 Results and Discussion

The electrokinetic behavior of *Scenedesmus acutus* is shown in Figure 3.3. The algae organism was found to be negatively charged above pH 4 and positively charged below pH 3, exhibiting a point of zero charge (p.z.c.) at pH 3.5. Results for *Chlorella vulgaris* were found to be quite similar, with the p.z.c. occurring at a slightly more acidic pH. These results illustrate that in the pH range used for cultivation of these organisms using coal fired flue gas as a CO_2 source (pH 5 to pH 8), the cells are negatively charged. Electrostatic repulsive forces are a primary mechanism preventing agglomeration from occurring. Adjustment of the pH to the p.z.c. would minimize electrostatic repulsion and natural flocculation would occur due to shorter range bonding forces, however, doing so on a large scale would be problematic. Recycling clarified water after sedimentation would require raising the pH to a range suitable for cultivation; precipitation of soluble nutrients may also occur. In addition, naturally flocculated algae cells would have a very low settling rate. The most desirable objective would be to induce flocculation at the natural pH of the growth system, producing flocs of sufficient size to achieve a rapid settling rate. A primary objective of this study was to evaluate the effectiveness of polymeric flocculants to achieve these objectives. Based upon the electrokinetic

behavior, cationic flocculants would be suitable additives. While nonionic and anionic flocculants can also induce flocculation of negatively charged algae cells due to polymer bridging effects, these additives were found to be ineffective, which is consistent with results reported by other researchers (McGarry 1970; Tenney et al. 1969).

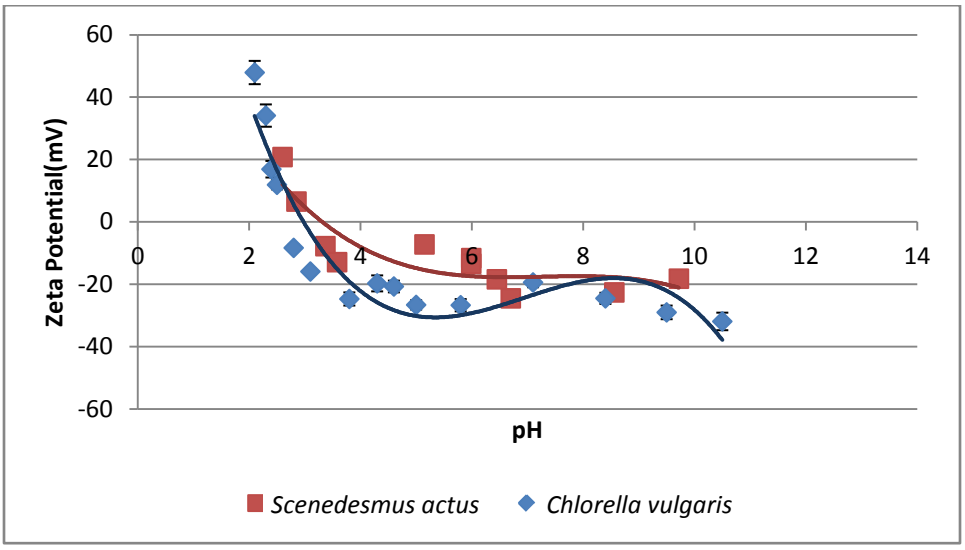

Figure 3.3: Zeta Potential versus pH for *Scenedesmus acutus* and *Chlorella vulgaris*.

The relationship of turbidity and dry mass concentration is shown in Figure 3.4. These results were obtained by measuring the turbidity of suspensions with varying algae concentrations and determining the dry mass concentration of the suspensions. Using this approach, clarified water quality can be estimated without determining the dry mass concentration of each clarified water sample.

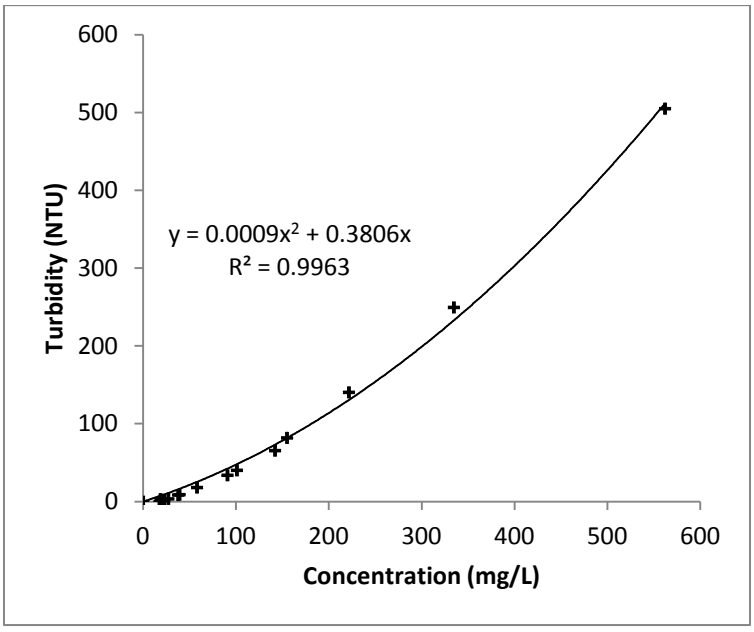

Figure 3.4: Relationship between algae concentration (n=3) and turbidity (n=5) with standard deviation bars (x,y < 7 units).

Results of settling tests conducted with cationic flocculants are shown in Figure 3.5. Using low MW 440 at a dosage of 40 ppm, 6.7 mL of settled biomass accumulated after 10 minutes and further accumulation of 10 mL occurred after 30 minutes. The supernatant contained 3.8 mg/L algae. Decreasing the dosage of the same flocculant to 20 ppm provided only 2.1 mL of settled biomass after 20 minutes of settling and no additional accumulation after 30 minutes. Using a higher molecular weight flocculant (540), 10 ml of biomass accumulated after 10 minutes with no further accumulation after 30 minutes, with excellent supernatant clarity (1.6 mg/L). At a lower dosage of 20 ppm, the higher MW flocculant provided only 3.8 ml of settled biomass. The medium MW 6702 flocculant provided no settled biomass. This is also confirmed by the NTU reading that correlates to 0.3 g/L for both dosage treatments. Alum was tested at a higher dosage for comparison with previous literature (Udaman et al. 2010; Sukenik et al. 1988). At a dosage of 100 ppm alum, 20 mL of biomass accumulated after 20 minutes and increased to a volume of 25 mL after 30 minutes. At a higher dosage of 200 ppm alum, 37 mL of biomass accumulated after 30 minutes. Two distinct differences in settling performance were evident when alum was used; the volume of biomass was significantly higher and supernatant clarity was much poorer in comparison with polymeric flocculants. Flocs formed with alum were fluffy and did not compact well. The resultant supernatant with alum contained 227 and 281 mg/L of suspended solids for alum treatments 200 ppm and 100 ppm respectively. This is significantly higher than what was achieved with polymeric flocculants. Approximately 75% of the biomass is left in the supernatant after 30 minutes with the best treatment of alum.

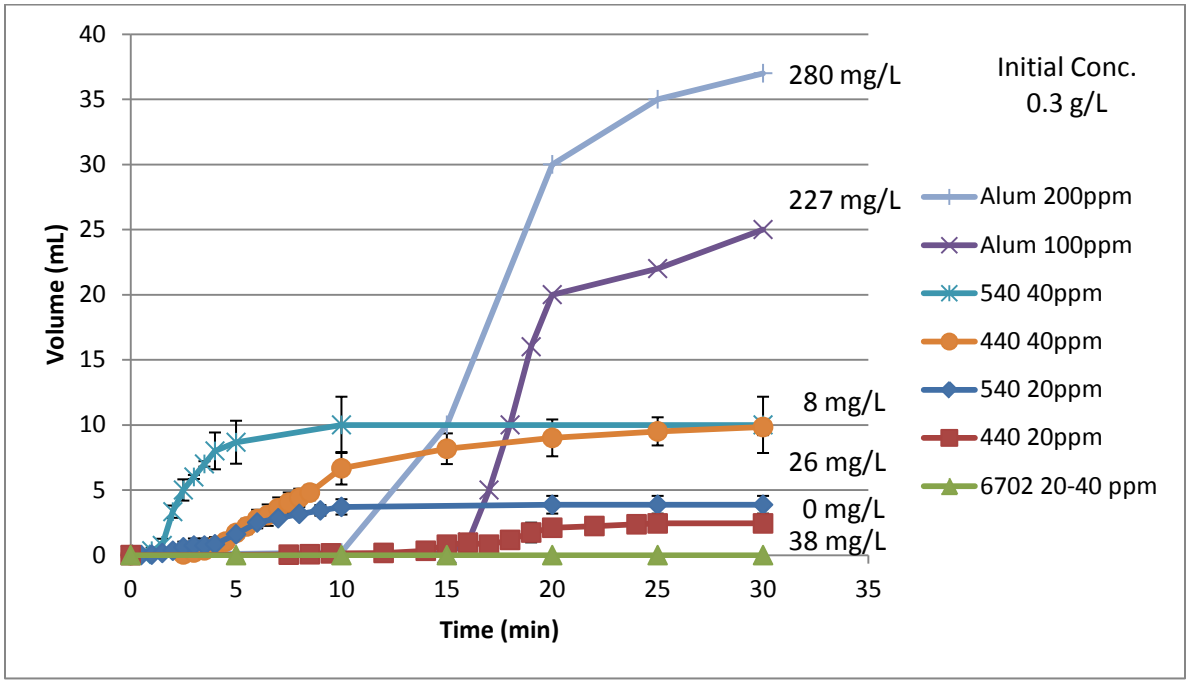

Figure 3.5: Settled biomass volume versus time for cationic flocculants for an initial concentration of 0.3 g/L. The values at the end of each curve represent the solids content in the water layer, estimated using the turbidity measurements (NTU). Error bars represent standard error (n=3).

Based upon the result shown in Figure 3.5, two flocculants appeared to be more effective for providing effective settling and high supernatant clarity; low MW 440 and high MW 540. A comparison of results achieved with these flocculants after 30 minutes of settling is shown in Figure 3.6. At a dosage of 20 ppm, the lower MW 440 provided higher compaction of settled solids than the higher MW 540 (10.7% solids versus 7.6% solids). However, turbidity was higher for the lower MW 440. At a higher dosage of 40 ppm, both flocculants provided similar compaction (i.e., 2.9% solids) and as with the lower dosage results, higher MW 540 provided clearer supernatant. While both of these flocculants provided acceptable results, it is evident that higher MW 540 provided better supernatant clarity. With respect to compacted solids, lower MW 440 provided better compaction at the lower dosage, presumably due to the formation of smaller flocs that provided better compaction.

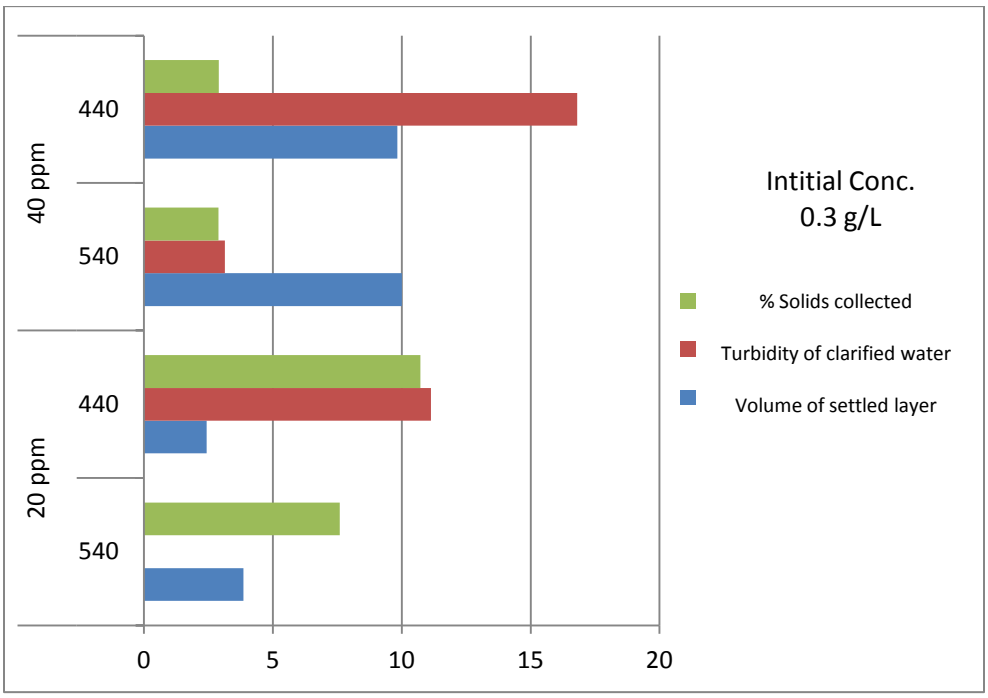

Figure 3.6: Settling results achieved with MW 440 and MW 540 flocculants after 30 minutes.

The MW 440 captures biomass that is denser at the 20 ppm dosage with over 10% solids in the settled layer. An ANOVA with a level of significance of 0.05 was performed on the % solids of the liquid cationic flocculants which is displayed in Table 3.2. The test determined that there is difference between the flocculant type and a very significant difference in the dosage used. However, algae cells are subject to wall effects in the tapered cone and wall effects become negligible as the container volume increases. At low dosage, some biomass adhered to the cone walls due to floc size and inhibited compaction. Increasing flocculant dosage created larger flocs via bridging effects and therefore created a larger volume of compacted solids. While the MW 440 may have

resulted in mildly higher % solids, the MW 540 was able to achieve similar values 66% faster (i.e. in 10 versus 30 minutes).

Table 3.2: ANOVA for the % solids for MW 440 and MW 540 flocculant at different dosages after 30 minutes.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*
Flocculant Type	7.48	1	7.48	5.59	0.04564
Dosage	117.37	1	117.37	87.78	1.38E-05
Interaction	7.26	1	7.26	5.43	0.04809
Error	10.70	8	1.34		
Total	142.81	11			

Figure 3.7 shows results obtained with varying culture densities (0.25, 0.547, and 1.012 g/L) using only high MW 540. For the lowest harvest culture density (0.25 g/L), a dosage of 5 ppm provided 7.3 mL of compacted solids. Increasing the dosage to 20 ppm reduced the volume of compacted solids to 5 ml. For a higher culture density (0.55 g/L), 10 ppm flocculant achieved 18.7 ml of solids which compacted to less than 10 mL at a higher dosage. With the highest culture density tested (1.0 g/L), 10 ppm provided 30 mL of settled solids with no appreciable further compaction at higher dosages. These result suggest that a dosage of 10 ppm is sufficient to provide settling of algal cells form culture densities as high as 1.0 g/L while higher dosages may provide further compaction. While it is intuitive that higher culture densities should require increased flocculant dosage to achieve acceptable settling performance, a dosage of 10 ppm appeared to be sufficient even when the culture density was increased from 0.25 to 1.0 g/L.

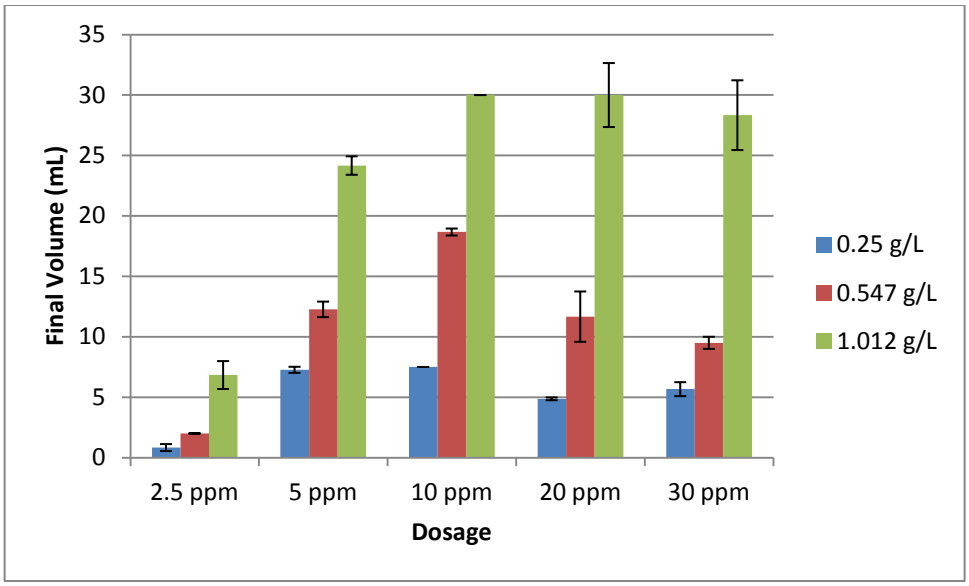

Figure 3.7: Final volume of the settled algae for flocculant MW 540 with various flocculant dosages (2.5, 5, 10, 20, and 30) and initial algae concentrations (0.25, 0.54, 1.012 g/L) after 20 minutes of settling. (n=3) showing standard deviation.

Results of high MW 540 at closer dosage intervals on a harvest culture density of 0.59 g/L are shown in Figure 3.8. The highest level of compaction was achieved with a dosage of 15 ppm which provided 16.3 mL of compacted solids (3.3% solids). Higher and lower flocculant dosages showed no evidence of additional compaction.

The volumes resulting in this experiment display a lower volume produced at 15 ppm due to compaction. The tabulated solids content data show a slight maximum. A dosage of 15 ±5 ppm could be selected to flocculate algae to be harvested from a culturing reactor of approximately 0.5 g/L. Performing ANOVA analysis on this test shows that there is a significant effect of dosage (Table 3.3).

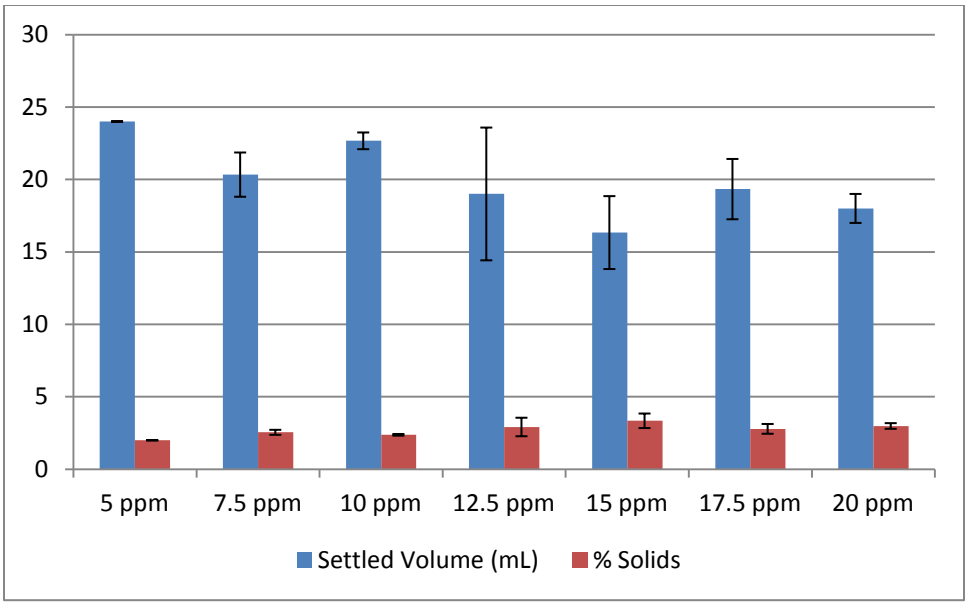

Figure 3.8: Effect of high MW 540 dosage on settled volume and calculated % solids for harvest concentration of 0.589 g/L. (n=3) showing standard deviation.

Table 3.3: ANOVA for the % solids in the bottom layer using MW 540 cationic flocculants at 7 dosage treatments.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*
Dosages	3.52	6	0.59	4.86	0.006999
Error	1.69	14	0.12		
Total	5.21	20			

When considering the 7 dosages, there is significant dosage effect. While the experiment in Figure 3.7 suggests that the ideal dosage should be 11.8 ppm, there is only slight improvement between 10 and 12.5 ppm. The ANOVA test was done again for the 10-15 ppm dosages and in this case, there were no statistical differences (Table 3.4) between the 10-15 ppm treatments at α=0.05. Therefore this dosage range could be effective for any harvest near 0.5 g/L.

Table 3.4: ANOVA for the % solids of settled material flocculated with MW 540 flocculant at 10, 12.5, and 15 ppm flocculant dosage treatments.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*
Dosage	1.411	2	0.707	3.20	0.1131
Error	1.33	6	0.221		
Total	2.74	8			

3.5 Conclusions

Liquid cationic polymers can flocculate microalgae cells, such that the algae flocs settle much faster than algae cells, resulting in an algae slurry (20-50 g/L) and water with low turbidity. The MW 540 flocculant aided the sedimentation of the algae to the bottom of the Imhoff cones; taking approximately 10 minutes for a total volume of 1 L. Successful sedimentation removed at least 90% of free water, therefore reducing thermal requirements for subsequent drying. In larger thickening vessels where wall effects are less influential, the slurry may potentially be subject to even higher compaction. Properly flocculated biomass could be further processed to extract even more water by mechanical means, such as filtration or centrifugation. Successful flocculation was done with a range of MW 540 flocculant dosages (5-30 ppm), effectively capturing algae harvests from dilute suspensions (0.25 and 0.55 g/L) up to a culture density of 1.0 g/L. This versatility can provide ease of service when utilized in field applications.

3.6 References

Bare, W.F.R., Jones, N.B., and Middlebrooks, E.J. 1975. Algae removal using dissolved air flotation. *Journal Water Pollution Control Federation*. 47(1):153-169.

Crofcheck, C., E, X., Shea, A., Montross, M., Crocker, M., and Andrews, R. 2012. Influence of media composition on the growth rate of *Chlorella vulgaris* and *Scenedesmus acutus* utilized for CO_2 mitigation. *Journal of Biochemical Technology.* 4(2):589-594.

EPA. 1987. Design manual, dewatering municipal wastewater sludges. *U.S. Environmental Protection Agency*. EPA/625/1-87/014 September:25-36.

Folkman, Y. and Wachs, A.M. 1973. Removal of algae from stabilization pond effluent by lime treatment. *Water Research.* 7(3):419-435.

Friedman, A.A., Peaks, D.A., and Nichols, R.L. 1977. Algae separation from oxidation pond effluents. *Journal of Water Pollution Control Federation.* 49(1):111-119.

Golueke, C.G. and Oswald, W.J. 1965. Harvesting and processing sewage grown planktonic algae. *Journal of Water Pollution Control Federation.* 37(4):47l-498.

McGarry, M.G. 1970. Algae flocculation with aluminum sulfate and polyelectrolytes. *Journal of Water Pollution Control Federation.* 42(5):R19l-R201.

Moraine, R., Shelef, G., Sandbank, E., Bar Moshe, Z., and Schwarbard, L. 1980. Recovery of sewage born algae: Flocculation and centrifugation techniques. In: Shelef, G. and Soeder, C.J. (Eds). *Algae Biomass: Production and Use*. Amsterdam-New York-Oxford: Elsevier/North-Holland Biomedical Press, 531-546.

Nigam, B.P., Ramanathan, P.K., and Venkataraman, L.V. 1980. Application of Chitosan as a flocculant for the cultures of the green-alga – *Scenedesmus Acutus*. *Archiv fur Hydrobiologie.* 88(3):378-387.

Noue, J.D.L. and Pauw, N.D. 1988. The potential of microalgal biotechnology: A review of production and uses of microalgae. *Biotechnology Advanced.* 6(4):725-770.

Pulz, O. and Gross, W. 2004. Valuable products from biotechnology of microalgae. *Applied Microbiology and Biotechnology.* 65(6):635-648.

Shelef, G., Sukenik, A., and Green, A. 1984. Microalgae harvesting: A literature review. SERI/STR-231-2396, UC Category: 61a, DE84013036.

Somasundaran, P. 1980. Principles of flocculation, dispersion, and selective flocculation. In: Fine Particle Processing: Proceedings of the International Symposium on Fine Particles Processing, Las Vegas, Nevada, February 24-28, v2. New York, NY: American Institute of Mining, Metallurgical, and Petroleum Engineers, 947-976.

Sukenik, A., Bilanovic, D., and Shelef, G. 1988. Flocculation of microalgae in brackish and Seawaters. *Biomass.* 15(3):187-199.

Tenney, M.W., Echelberger, W.F., Schuessler, R.G., and Pavoni, J.L. 1969. Algal flocculation with synthetic organic polyelectrolytes. *Applied Microbiology.* 18(6):965-971.

Uduman, N., Qi, Y., Danquah, M.K., Forde, G.M., and Hoadley, A. 2010. Dewatering microalgal cultures: A major bottleneck to algae- based fuels. *Journal of Renewable Sustainable Energy.* 2(012701):1-15.

CHAPTER 4 EVALUATION OF FILTRATION FOR DEWATERING OF ALGAL BIOMASS

Nicholas Rhea, Jack Groppo, and Czarena Crofcheck

4.1 Summary

As algae can be used as a feedstock for agricultural fertilizers, livestock/poultry feeds, anaerobic digestion, and biofuel production. Regardless of the end product, water removal is necessary and difficult to do cost effectively. For each product the requirements for moisture content (or solids content) vary, such that a desirable water removal strategy would need to be adaptable to varying levels of water removal. Flocculation, with sedimentation and drying was evaluated as a possible strategy for algae dewatering. Cationic flocculants have been investigated in the previous literature performed on algal biomass. Solids were successfully separated as a cake through vacuum filtration and rates were evaluated. Filtration rates of *Scenedesmus actus* were measured on algae slurry treated with 10 to15 ppm of a synthetic cationic polymeric flocculant (Chapter 3). The results of this study should assist in predicting the time it takes to filter flocculated algae slurry at a concentration range of 15.0-50.0 g/L to a product at a concentration range of 50-250 g/L.

KEYWORDS: algae, flocculation, filtration, dewatering, thickening, sedimentation

4.2 Introduction

Many algae species have been used as a food source, nutritional supplement, food additive, pharmaceutical, cosmetic, animal feed, and have potential as biofuel/energy (Pulz and Gross 2004). Kelp, a brown algae, is a prominent ingredient in Asian cuisine. Some strains of *Spirulina* and *Chlorella* are marketed as health foods (Noue and Pauw 1988). Compounds such as β-carotene can be extracted for vitamins. Much interest in algae is due to what they contain. Some strains of microalgae may contain elevated concentrations of polysaccharides, proteins, or lipids. They may be processed for different applications, depending on which organic compounds are present.

The utilization of algae as a feedstock for alternative fuel source and also as mitigation for CO_2 has the potential to address many energy and environmental problems. One problem is harvesting and retrieving algal biomass. In particular, dewatering processes are a major hindrance in employing algae systems. For large amounts of CO_2 mitigation, large amounts of algae must be grown. That algal biomass will need to be harvested continuously habitually to maintain an operating system. Algae is said to be harvested whenever the dilute suspension of 0.02-0.06% TSS (total suspended solids) is collected and then conditioned to 5-25% TSS or higher (Shelef et al. 1984). Culturing systems are typically a dilute suspension of microscopic cyanobacteria, formally referred to as blue-green algae. Processes downstream demand only the algal biomass and not the huge volume of water that follows.

Since there is such a large burden to remove water from algal biomass, one technology suggested is to use flocculation to remove algae from suspension. This process actually makes the cells susceptible to other handling techniques. Using some secondary

thickening process is required for higher solids. Other thickening equipment under speculation is centrifugation, pressure filtration, vacuum filtration, flotation, and many more. Thickening means that the viscosity of a substance is increased by reduction, or some means of water/liquid removal. Dewatering is the removal of water from solids in a mixture by these and other types of wet classification.

Harvesting biomass is necessary to maintain the algae culture density (0.4-1.0 g/L) for most bioreactors and allows for the recycled water to be sterilized, thereby reducing contamination. The harvesting system includes flocculation, sedimentation, and filtration (Figure 4.1). These unit operations were selected because they are standard thickening processes that are used in commercial applications, such as wastewater treatment and mineral processing (EPA 1987). Thickened slurry (20-50 g/L) from the process enables direct utilization of algae for methane production via anaerobic digestion. Further dewatering by gravity filtration produces an algae paste (80-120 g/L) amenable to wet lipid extraction for biodiesel production. Other potential utilization options, such as biodiesel production via dry lipid extraction or bioplastic production, require moisture reduction to levels that can only be achieved by thermal drying (i.e. <10% moisture). While thickening and filtration cannot achieve these moisture levels, they are essential steps for removing a substantial amount of water prior to applying thermal processes.

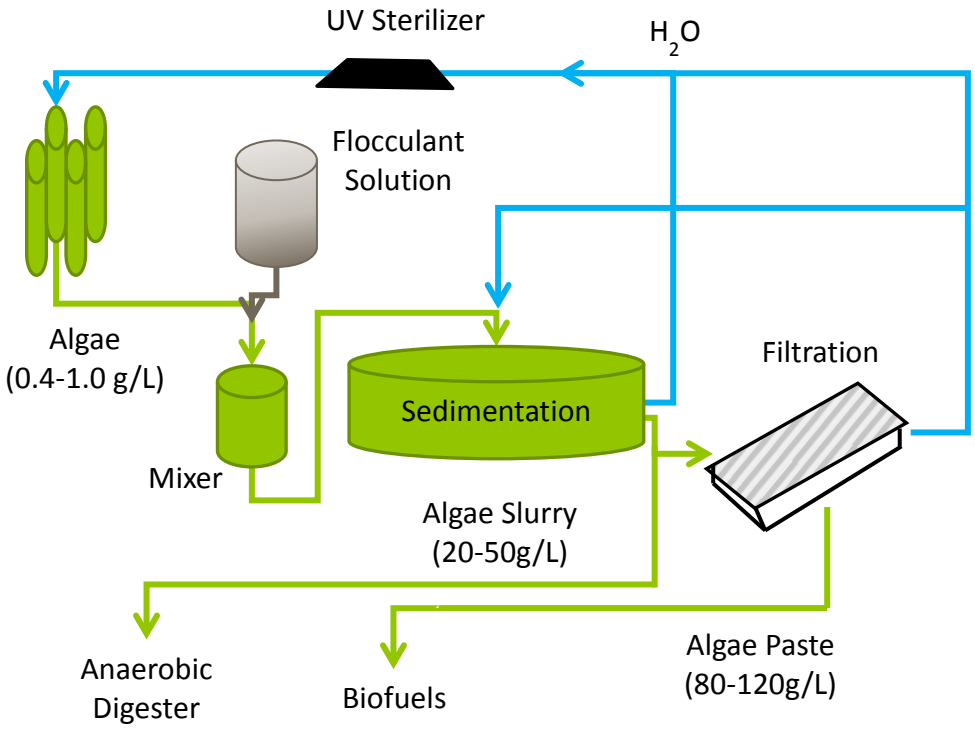

Figure 4.1: Algae harvest process diagram showing sedimentation and filtration.

The goal of this work was to evaluate the processing conditions required for thickening harvested algal biomass to the consistency requirements for further utilization, while simultaneously providing acceptable clarified water quality to enable recycling of soluble

nutrients as well as minimizing water consumption. Determination of process conditions required for effective filtration performance will confirm the plausibility of using these standard industrial techniques to dewater large scale algal biomass. The specific objectives include selection of the appropriate filtration media and evaluation of filtration performance on flocculated biomass proposed in the previous study. This study will focus on macrofiltration techniques known as wet cake filtration driven by atmospheric-driven (gravity-only) and vacuum-driven pressure gradients.

The microalgae used in this study (*Scenedesmus actus*) was cultivated in airlift photobioreactors (PBRs) utilizing sparged CO_2. Individual cells of the organism are approximately 5 µm in size, contain 80% intercellular water and have a density of ˜1.0 g/mL. Dry mass concentration of the organism in the PBR is dependent on growth conditions and periodic harvesting is necessary to maintain a culture density <0.3 g dry weight/L to minimize photoinhibition. Harvesting consists of removing a significant portion of the PBR system volume (typically 80%), separating the algae cells from the process water via sedimentation, and recycling clarified water and soluble nutrients back to the PBR to dilute the remaining culture for another growth cycle. Given the small size and low density of the algae cells, microfiltration is a very slow process, thus identifying the parameters and investigating filtration rate was the focus of this investigation.

Algae biomass is very difficult to dewater with standard separation technology and equipment since its density is so close to the water it is suspended in. The cells have very little to no structural rigidity, which limits the magnitude of force that can be applied before deformation or shear overwhelms the cells. These problems have been noted in previous work with algae centrifugation (Divakaran et al. 2001) and algae pressurized filtration (Sim et al. 1988). Efficiency could potentially be improved through utilization of cationic polymeric flocculants proposed in the previous study; however floc structure integrity is unknown under high velocity/shear equipment. Operational expenses of centrifugation shadows the savings potential of filtration systems. Physical constraints of algae biomass also make the viability of filtering difficult to identify and restricting applications from using pressure gradient assistance. Filtering unflocculated cells also limits pore spacing to less than 5 µm and severely impacts air velocity parameters thus slowing down process time, as seen in microfiltration under laboratory settings. On the dry biomass route, spray dryers (Shelef et al. 1984) could be used to efficiently remove all moisture. Other options attempted are unproven in large scale applications such as electro-coagulation (Vandame et al. 2011) and froth flotation (Chen et al. 1998). However, mechanically removing free water would reduce emissions and cost associated with heating energy demand.

Polymeric cationic flocculants have proven to be effective at capturing algae cells from suspension into concentrated slurry. This slurry could then be further processed to extract additional free water with cake filtration practices. Filter media must be appropriately sized to support an established cake as well as any elevated pressure gradient to increase filtrate throughput. The absence of supporting literature corroborates the necessity of investigation in performance evaluation that could forecast processing potential and sizing of algae filtration systems. Processing parameters such as cake thickness, feed concentration, air velocity; controlled by pressure, and rate of filtration in grams/m^2/min are important considerations for filtering algae at large scale.

In this work, algal biomass was treated with a 10-15 ppm dosage of cationic synthetic polymer and after sedimentation was processed across multifilament filter fabric under vacuum. The goal of this study was to validate that algae cells treated by such means could indeed be processed by vacuum belt filters and under what conditions could the solids content be increased to 5 to 25 wt%. It was hypothesized that a feed slurry at 1.5 to 5.0 wt% can be conditioned to a range of 5.0-10.0 wt% under gravity filtration and further increased to 10.0 to 25.0 wt% under vacuum filtration. Processing parameters such as cake formation time, filtration rate, and mass throughput were evaluated against variables such as cake thickness, feed concentration, and processing time.

4.3Materials and Methods

4.3.1 Algae cultivation

Scenedesmus actus microalgae was cultured with the procedures, given by Crofcheck et al. (2012), demonstrated in the previous chapter. Biomass was transferred from airlift reactors to seed a ~4,000 L bioreactor. Whenever the culture density exceeded 0.4 g/L dry mass concentration, a harvest volume of 1,000 L would be withdrawn from the reactor and treated with 10 ppm of Zinkan 540 cationic polyacrylamide flocculant and mixed. Both can be found in Figure 4.2. The additive was given 16 hours to ensure sedimentation was complete. Supernatant would then be decanted from the tank, leaving ~20 L of algae slurry at ~50 g/L concentration for sample in filtration work.

Figure 4.2: Algae bioreactor and harvest tank for flocculation.

4.3.2 Filtration set-up

A 102.58 cm^2 filtration vessel seen in Figure 4.3 with the capability of vacuum or pressure application was utilized in the experiments. The ring (1) and backing cloth (2) were placed onto the stand to provide separation volume between the filter media (3) and the stand drain. This spacing prevents adhesion to the vessel and allows for proper pressure gradient across the entire cross sectional area of the filter media. The backing cloth has legs to ensure the filter media is flush with the ring and allows for even pressure distribution with no sagging. A media, washed and pre-wetted for each individual test, was then placed on top of the ring and backing cloth. The cylinder (4) was placed on the filter fabric thus completing the assembly. Thumb knobs were used as clamping force to provide a seal between the o-rings on the stand and cylinder. This entire assembly was then positioned over a beaker and balance to capture and weigh filtrate mass. When

required, a vacuum pump was connected to the drain via a vacuum Erlenmeyer flask with tubing and a fitted rubber stopper.

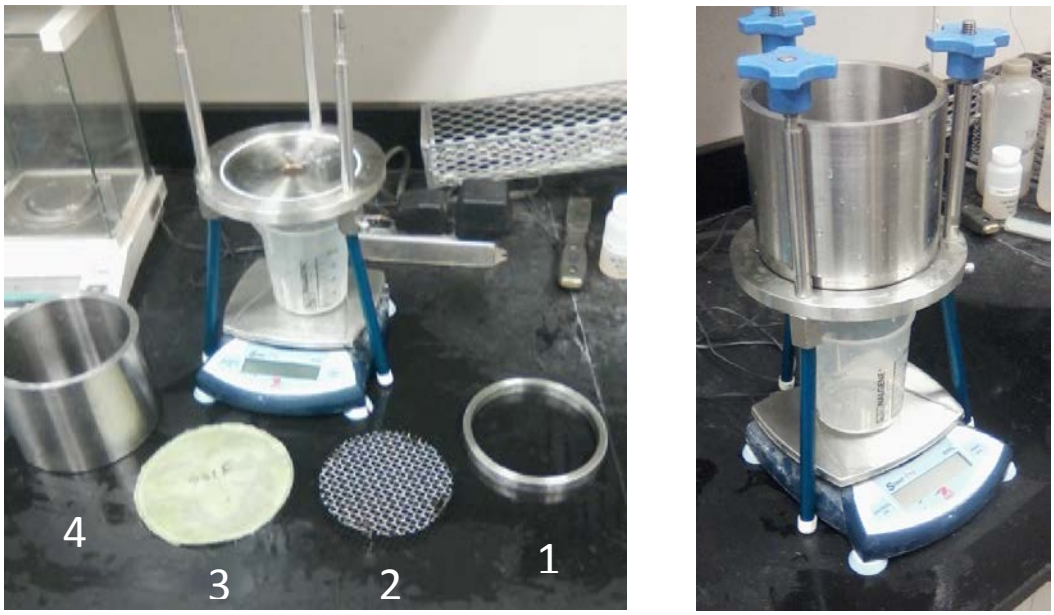

Figure 4.3: The filter apparatus is assembled for each test and positioned over a beaker with a balance to measure filtrate mass passing the filter media, 1) ring, 2) backing cloth, 3) filter media, and 4) the cylinder.

4.3.3 Filter medium selection

Selection of appropriate filters are imperative to throughput and capture efficiency for 5 µm algae cells that are pliable due to their high intracellular water content, ~80%, and density, ~1.05 g/mL. Pressure gradients cause concern. Two filter mediums, 929M and 901F, were considered for filtering flocculated algae (Figure 4.4). The 929M filter media is comprised of rigid polyethylene monofilaments woven in a 2 over 1 pattern which leaves openings in the fabric. The 901F filter media is manufactured in with multiple strands of polypropylene fiber multifilament bundles woven in a 1 over 1 pattern.

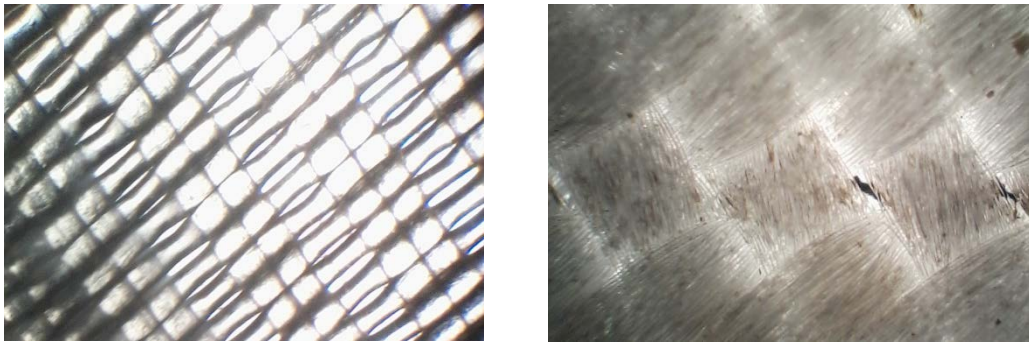

Figure 4.4: Two filter medium used for filtration at 40x magnification. Left: Monofilament 929M. Right: Multifilament 901F.

Each fabric was tested using 200 mL of slurry at a concentration of 47 g/L. Both tests were allowed to drain by gravity for 5 minutes before applying vacuum of nearly 20 in

Hg for 1 minute. The filtrate mass were recorded for each experiment and then filtered with Whatman #1 paper and dried at 100 °C for 24 hour to estimate the algae passing through the filter, which represents the amount of algae lost in the experiment. The residue on the filter medium was collected and dried at 100°C to calculate the wt% of solids of the filter cake, the amount of algae collected in the experiment.

4.3.4 Filtration tests

Gravity

Filtration studies by gravity were performed on 901F multifilament fabric. In one design of experiments, the concentration of algae slurry was held constant at 28.3 g/L while varying the feed volume at 200, 300, 400, and 500 mL. Filtrate mass was recorded over a 60 minute time period. Cake thickness was measured with a pair of digital Vernier calipers. The wet cake was removed from the filter medium, weighed for wet weight, dried at 100°C, and reweighed for dry weight. The filter medium would be washed with a bottle brush and rinsed between each trial. The original sample of algae would be gently mixed before each trial.

In another design of experiments, the volume of feed slurry was held constant at 400 mL while varying the feed concentration. This was accomplished by diluting the total volume of sample after each trial to obtain 50, 40, 38, 30.5, and 30 g/L concentrations. Filtrate mass was recorded over a 60 minute time period. Cake thickness was measured with a pair of digital Vernier calipers. The wet cake would be removed from the filter fabric and weighed with a four place balance for gross wet weight, dried at 100°C, and reweighed for dry net weight. The fabric would be washed with a bottle brush and rinsed between each trial. The original sample would be gently mixed before each trial.

Vacuum

Filtration studies with vacuum assistance were performed on 901F multifilament fabric. The vacuum applied would depress the thickness of the cake to which the variations would not be distinguishable. Two variables were taken into consideration, time of gravity filtration and feed concentration of slurry. Feed volume was held constant to 400 mL as well as the duration of vacuum at 1 minute. Gravity filtration cycles were 0, 3, 5, 7, 10, and 15 minutes. Feed concentration would be altered by diluting the original sample with water. Filtrate mass was recorded over the trial duration. The wet cake would be removed from the filter fabric and weighed with a four place balance for gross wet weight, dried at 100°C, and reweighed for dry net weight. The fabric would be washed with a bottle brush and rinsed between each trial. The original sample would be gently mixed before each trial. The limited supply of sample from each harvest dictated the design of the vacuum experiment to ensure that each trial was performed on the same healthy culture and used within 3 days.

4.4 Results and Discussion

4.4.1 Filter medium selection

During gravity filtration, 901F multifilament fabric had a higher filter rate at 8 g/min compared to 5 g/min for the 929M monofilament fabric (Figure 4.5). After a vacuum

was applied, the monofilament allowed 25 g to pass through. Figure 4.6 shows the calculations of cake solids and capture efficiency calculated from the weight measurements of the cakes and filtrates before and after drying. While both cakes contain approximately the same solid content, the 901F multifilament was more effective at capturing mass. Whenever pressure was added to the monofilament fabric (929M), the cake was unable to withstand the pressure gradient and biomass was pulled through the openings. The cake contained 14.8 wt% solids but only 68.2% of the slurry mass had been captured. The cake was supported on the multifilament without being pulled through the tight bundles of fiber weave. The filtrate of the multifilament had a nearly immeasurable mass on a Whatman #1 and the turbidity was less than 5 NTU or 10.5 mg/L, so the capture efficiency was considered to be greater than 99%.

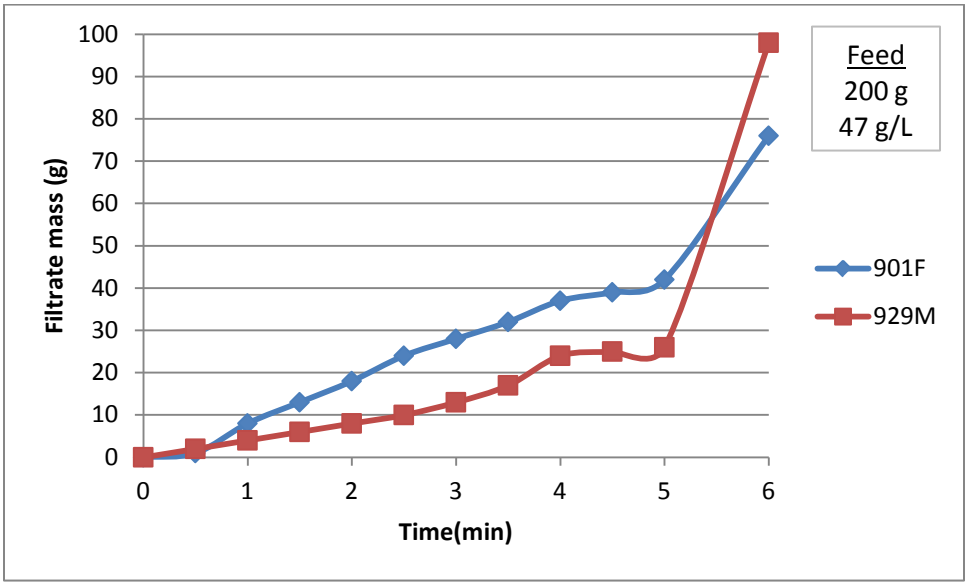

Figure 4.5: Filtrate mass throughput for two different filter mediums (901F and 929M) as a function of time, where from 0 to 5 minutes only gravity was used and from 5 to 6 minutes vacuum was applied. The initial feed weight, 200 g, and concentration, 47 g/L, was held constant.

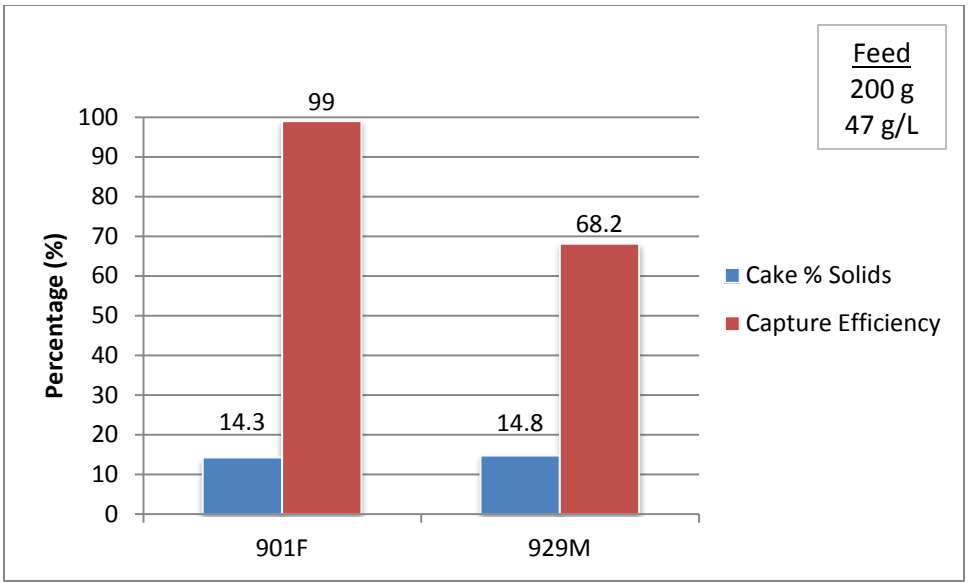

Figure 4.6: Comparison of the two different filter mediums (901F and 929M) with respect to Cake % solids and capture efficiency as a function of time, where from 0 to 5 minutes only gravity was used and from 5 to 6 minutes vacuum was applied. The initial feed weight, 200 g, and concentration, 47 g/L, was held constant.

4.4.2 Filtration test

Gravity

Filtrate throughputs of gravity filtration with variable feed volumes are shown in Figure 4.7. Cake thickness is a controllable variable that could impact filtration rate. The 16.5 mm cake was nearly 2.5x thicker than the smallest volume introduced to the test which would correspond to the 2.5x increase in slurry volume introduced carrying 2.5x more biomass given the feed concentration was constant. The filtrate ratio, *mass of filtrate/mass of feed*, was approximately 0.61 for the thickest cake and 0.55 for the thinnest cake. This could indicate higher head pressure pushing more free water through the interaction plane or suspect signs of mild turbulence upon introduction into the testing apparatus which allow more water to evacuate before a cake could properly form. Cake formation time, typically seen as a sharp inflection of throughput under vacuum or pressure on denser suspensions, is defined as the time at which the filtration rate (dV/dt) approaches 0. At this point, liquid can no longer freely migrate around deposited and suspended solids and must percolate through an established solid cake. The cake formation time appears at approximately 5 minutes and 15 minutes for the thinnest and thickest cake, respectively. The theoretical biomass volumetric throughput would be 13.7 mL/min for the thinnest cake versus 11.2 mL/min for the thickest cake. This supports that a thinner cake would form faster leading to higher belt and rotational speeds on corresponding belt and drum filters.

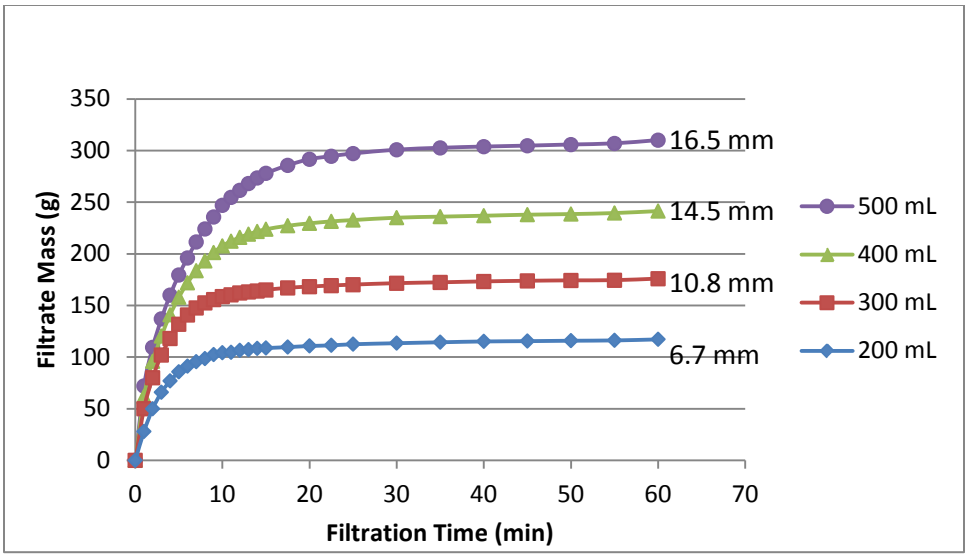

Figure 4.7: Gravity throughput for varied feed volumes with a constant feed concentration 28.3 g/L of slurry with large discrepancy in cake thickness (final cake thickness showed at the end of each curve).

While a thinner cake supports the theory of higher throughput by volume, Figure 4.8 shows the calculated cake solids wt% after the final cakes were dried and weighed removing residual and bound moisture. After 60 minutes, the thinnest cake contained 7.5% algae solids by weight while the thickest cake contained 8.8% solids by weight. With the density of algae and water assumed to be equal, biomass throughput rate would be 1.03 g/min and 0.98 g/min for the thin and thick cakes respectively in this experiment. Thinner filtration cakes might have a slight advantage; however an error of 0.1 mm could result in nearly 0.08 g of error in the biomass throughput rate demonstrating that slurry feed volumes was not a crucial factor the tests.

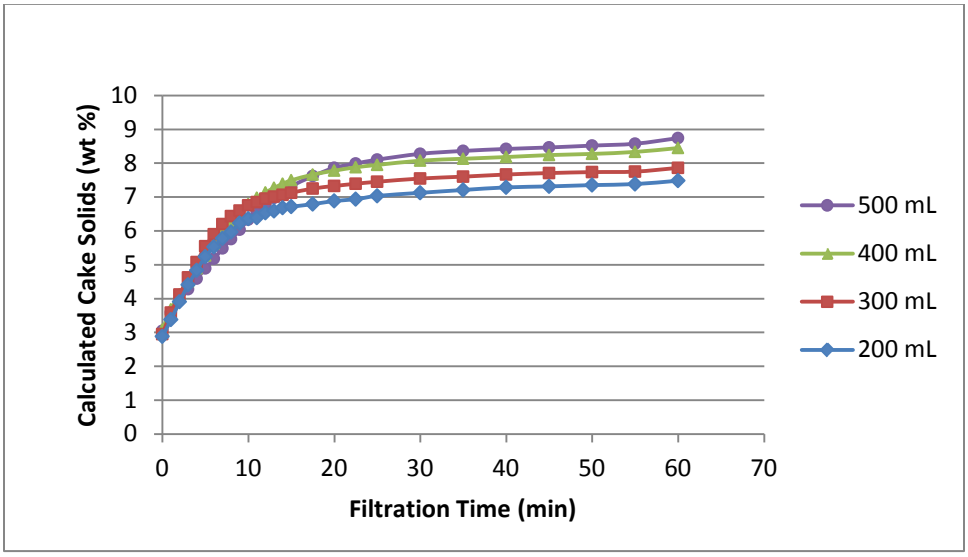

Figure 4.8: Cake % solids as a function of filtration time for varied feed volumes with a constant feed concentration of 28.3 g/L with gravity assisted filtration.

Figure 4.9 shows the amount free water that would be remaining in the sample assuming that there is 80% intercellular water bound within the *Scenedesmus actus* species. The moisture content of the cake would be 92 wt% however 73% would be bound within the cells, *bound water mass/total cake mass*. Approximately 65-75% of the free water in the slurry was removed with gravity filtration alone in 20 minutes or less.

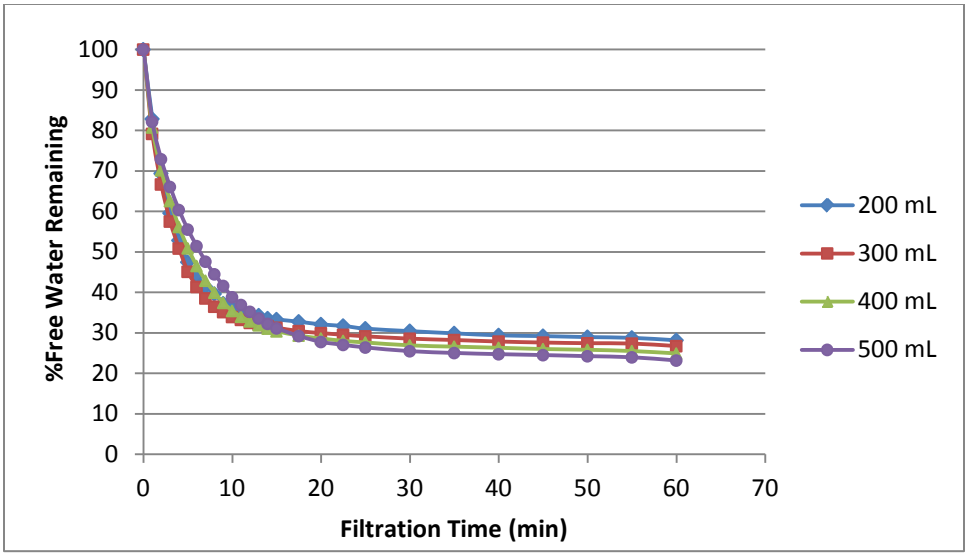

Figure 4.9: Free water percentages remaining for varied feed volumes with a constant feed concentration of 28.3 g/L slurry with gravity assisted filtration.

Filtrate throughputs of gravity filtration with variable feed concentrations are shown in Figure 4.10. The 50 g/L concentration produced a cake of 20.0 mm while 30.25 g/L produced a cake thickness of 15.65 mm. The thicker slurry was approximately 1.65x concentrated while the thickness was only increased by approximately 1.27x. The filtrate ratio was 0.5 and 0.3125 for the thinnest and thickest cake, respectively. The cake formation time appears at approximately 8 minutes and 15 minutes for the thinnest and thickest cake respectively. The theoretical biomass volumetric throughput would be 19.9 cm^3/min for the thinnest cake versus 13.6 cm^3/min for the thickest cake. Again the thinner cake could yield higher linear and rotational throughput speeds.

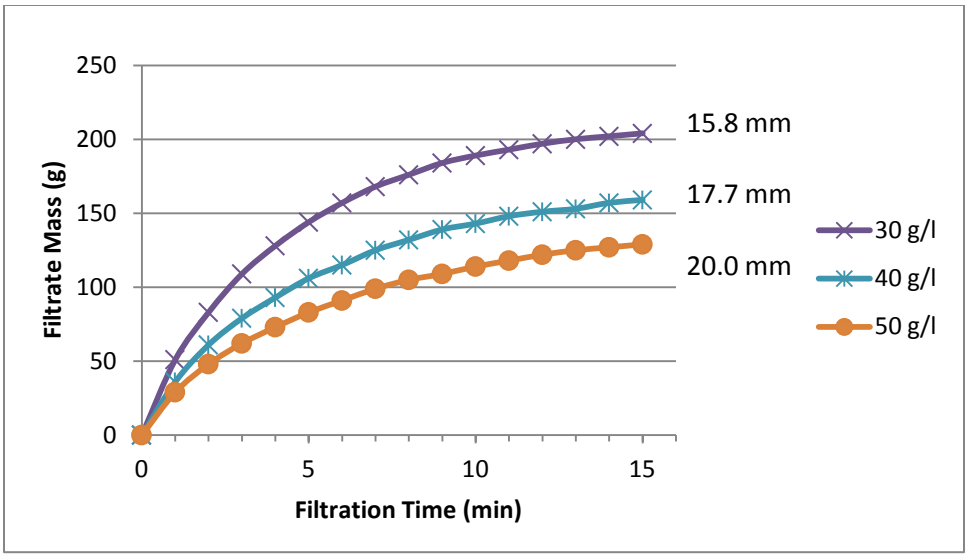

Figure 4.10: Gravity throughput for varied feed concentrations for a constant feed volume of 400 mL of slurry with small discrepancy in cake thickness.

Figure 4.11 shows the calculated cake solids wt%. After 15 minutes, the thinnest cake contained 7.0% algae solids by weight while the thickest cake contained 8.0% solids by weight. With the density of algae and water assumed to be equal, biomass throughput rate would be 1.39 g/min and 1.09 g/min for the thin and thick cakes respectively in this experiment. Thinner filtration cakes might have a slight advantage when they are produced from less concentrated feed slurry.

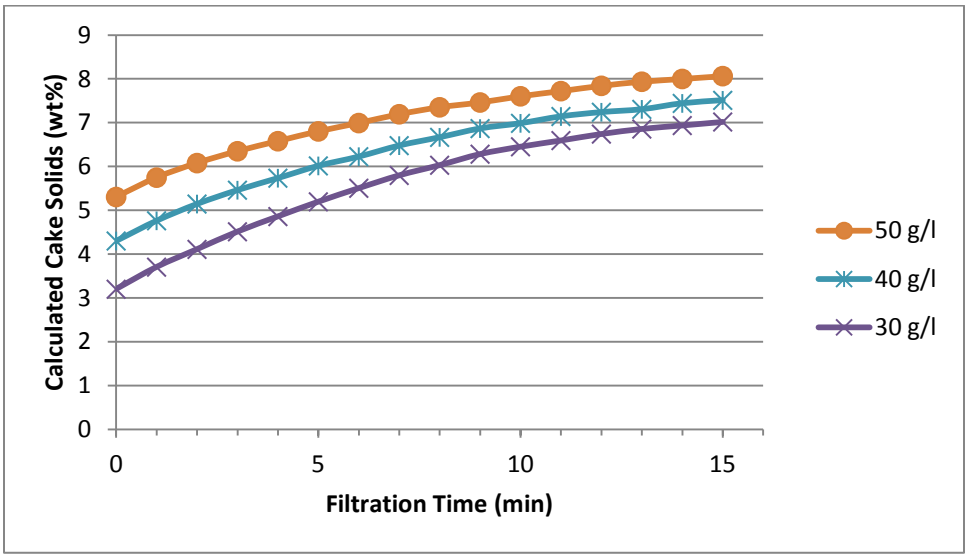

Figure 4.11: Cake solids over the course of filtration for varied feed concentrations for a constant feed volume of 400 mL of slurry with gravity assisted filtration.

Vacuum

Higher pressure gradient was achieved with vacuum assistance. Figure 4.12 displays the filtrate throughputs of 6 cycle times of gravity filtration and 1 minute vacuum application

for independent trials with 400 mL of constant feed slurry concentration, 31.4 g/L. Nearly 200 g of filtrate was removed with 1 minute of vacuum filtration, which is approximately 50 grams less than 15 minutes of gravity filtration. An extra 50+ grams of filtrate is evacuated when the cake has freely drained for at least 7 minutes, which would be the approximate cake formation time at this feed slurry concentration. The 16 minute cycle time would produce a volumetric throughput rate of 6.25 mL/min. No solids passed the fabric for any trial, even when no gravity drainage had occurred. This insinuates that a gravity section of the belt may not be required to establish a cake using the 901F (multifilament) medium. It is plausible that industrial vacuum processes would be able to handle this biomass. With 2-3 minute vacuum application, 300 grams of free water would possibly be removed of this 400 mL volume. However, this parameter was held at 1 minute to limit the number of dependent variables because of scarce original sample.

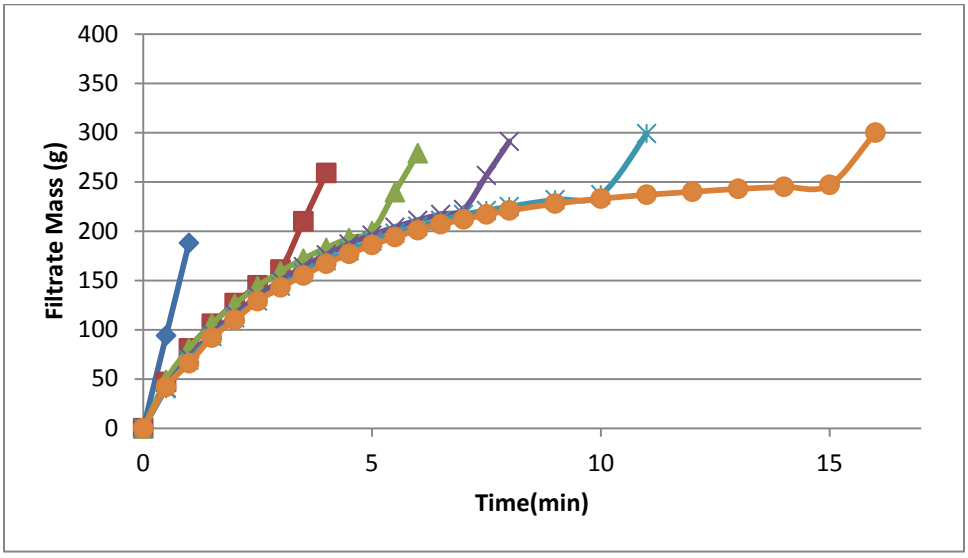

Figure 4.12: Throughput over the course of filtration for varied cycle times for one minute vacuum with a feed concentration of 31.4 g/L.

Figure 4.13 shows the calculated cake solids wt% for the six cycle times in the previous trial. After the cake is theoretically fully formed at 7 minutes under gravity, the cake solids were improved by over 80% at the eight minute of the total cycle. The 16 minute cycle time only improved the cake solids by 50%, but the overall cake solids were approximately 16 wt%. This shows that fully formed cakes can be dried mechanically with short durations of vacuum application. The biomass throughput rate would be 1.0 g/min at the 16 minute cycle time. Airflow velocity through the filter fabric could influence these rates as well as dryness.

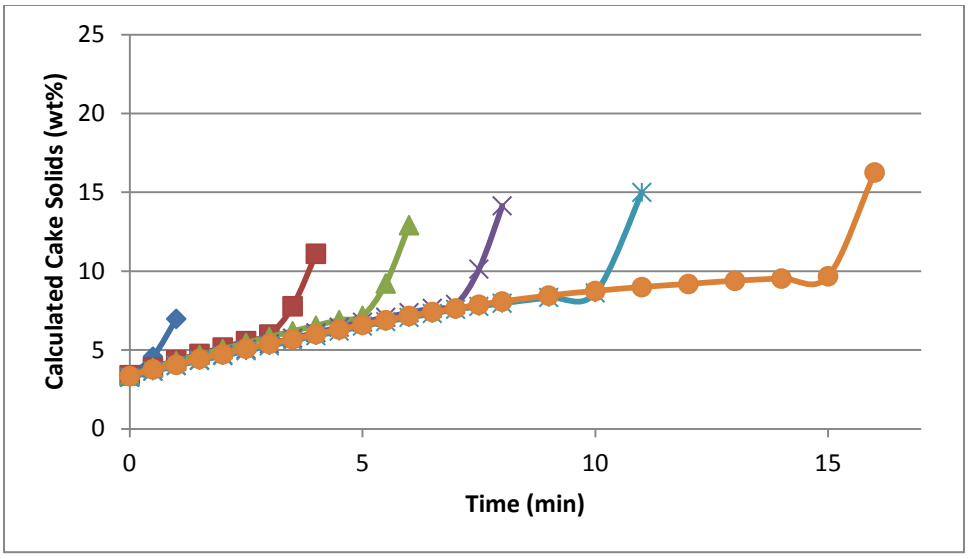

Figure 4.13: Cake solids tabulated for varied cycle times showing elevated solids content with vacuum for a feed concentration of 31.4 g/L.

The previous experiment was repeated for varying feed slurry concentrations. Figure 4.14 shows the final cake solids for each cycle time with varying feed slurry concentrations up to 32 g/L. The results indicate that under identical test parameters there is an optimal feed concentration of 10-20 g/L that would produce the driest cake. The 16 minute cycle time at 15 g/L could be due to any number of errors instigated by original sample mixing, filter fabric cleanliness, et al. The 11 minute cycle time at this concentration would theoretically yield 0.7 g/min. No gravity drainage pulled the same volume of filtrate therefore theoretically producing at a rate of 6.6 g/min.

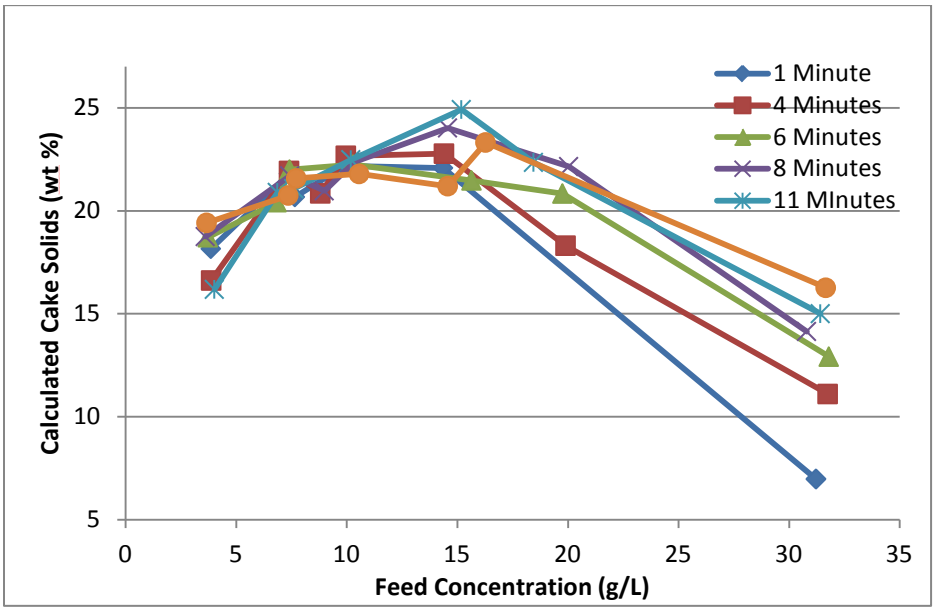

Figure 4.14: Final wt% of all tested concentrations corresponding with cycle time showing an optimal feed concentration range of 10-20 g/L (Gravity w/1' Vacuum).

4.5 Conclusions

When coupled with flocculation by liquid cationic polymers, algae cells can be conditioned in such a way that they are able to be processed using industrial scale filtration systems. Multifilament filter media, like 901F, can withstand the higher pressure gradient of vacuum assistance. Other industrial filter fabrics and media could have similar success. Gravity filtration work suggested that thinner cakes would deliver slightly higher mass throughputs. The maximum solids content of cakes produced in this study was 25 wt%. This is nearly double the content of algal biomass produced by disk stack centrifugation which delivers a maximum of 12 wt% (Uduman et al. 2010). For products requiring thermal upgrading, filtered algae biomass would reduce the evaporation requirements by 380 MJ/tonne. Other solids content ranges could be obtained by altering filtration cycle times, pressures, and other parameters to meet the requirements of products along the wet biomass route. With considerations of the experiments conducted during this study, a maximum production rate of 66 $kg/m^2/min$ per dry basis could be obtained on slurry at 15 g/L feed concentration with a 901F filter fabric under vacuum. Vacuum drum or belt filters could be appropriately sized for large scale algae culturing programs to condition harvests towards a plethora of various end-use products.

4.6 References

Chen, Y.M., Liu, J.C., and Ju, Y.H. 1998. Flotation removal of algae from water. *Colloids and Surfaces B: Biointerfaces.* 12(1):49-55.

Crofcheck, C., E, X., Shea, A., Montross, M., Crocker, M., and Andrews, R. 2012. Influence of media composition on the growth rate of *Chlorella vulgaris* and *Scenedesmus acutus* utilized for CO_2 mitigation. *Journal of Biochemical Technology.* 4(2):589-594.

Divakaran, R. and Sivasankara Pillai, V.N. 2002. Flocculation of algae using chitosan. *Journal of Applied Phycology.* 14(5):419-422.

EPA. 1987. Design manual, dewatering municipal wastewater sludges. *U.S. Environmental Protection Agency*. EPA/625/1-87/014 September:25-36.

Noue, J.D.L. and Pauw, N.D. 1988. The potential of microalgal biotechnology: A review of production and uses of microalgae. *Biotechnology Advanced.* 6(4):725-770.

Pulz, O. and Gross, W. 2004. Valuable products from biotechnology of microalgae. *Applied Microbiology and Biotechnology.* 65(6):635-648.

Shelef, G., Sukenik, A., and Green, A. 1984. Microalgae harvesting: A literature review. SERI/STR-231-2396, UC Category: 61a, DE84013036

Sim, T.S., Goh, A., and Becker, E.W. 1988. Comparison of centrifugation, dissolved air flotation and drum filtration techniques for harvesting sewage-grown algae. *Journal of Biomass.* 16(1):51-62.

Uduman, N., Qi, Y., Danquah, M.K., Forde, G.M., and Hoadley, A. 2010. Dewatering microalgal cultures: A major bottleneck to algae- based fuels. *Journal of Renewable Sustainable Energy.* 2(1):1-15.

Vandamme, D., Pontes, S.C.V., Goiris, K., Foubert, I., Pinoy, L.J.J., and Muylaert, K. 2011. Evaluation of electro-coagulation-flocculation for harvesting marine and freshwater microalgae. *Biotechnology and Bioengineering.* 108(10):2320-2329.

CHAPTER 5 CONCLUSIONS AND FUTURE WORK

This goal of this work was to evaluate the ability flocculation, sedimentation, and filtration to dewater and thicken algae from a dilute culture using low energy mechanical methods. Since most microalgae cells contain a fair amount of water, mechanical dewatering is only effective at removing free water, when the cells are not lysed. If cells remain intact, the maximum solid weight percentage of mechanically thickened biomass is approximately 25-30 wt%. In terms of algae harvesting, the goal would be to maximize the amount of algae recovered and minimize the amount of algae left in the clarified water portion, while also achieving the separation in the shortest amount of time. Hence, there is a balance of interconnected operating parameters that must be evaluated. In addition, considering the large amount of algae culture that would need to be harvested, throughput is another important consideration. Finding a recovery strategy that is compatible with current large scale recovery methods, such as gravity thickeners and belt filters would be beneficial in the long run.

Flocculation followed by sedimentation of algae cells was evaluated as a possible strategy utilizing cationic polymeric flocculants (Chapter 3). Liquid polyacrylamides appear to be very successive coagulants, specifically higher molecular weight. Small dosages of cationic polymeric flocculant, 5-20 ppm, are required coagulate the cells as opposed to 100-200 ppm of natural flocculants such as Alum. Large flocs are generated within a few minutes of low shear mixing. Such flocs are able to settle immediately leaving a relatively clean supernatant. Settling with the Imhoff cones occurs in a few minutes; taller vessels with suitable coalescence would most likely settle quickly as well. The 540 flocculant was able to flocculate *Scenedesmus acutus* at concentrations up to 1.0 g/L with 10 to 15 ppm dosage. It is nearest this range at which the most compacted solids are observed such that the slurry concentrated is maximized. Further work could be performed to optimize the dosage requirements at various concentrations such that a recommendation for algae flocculation would be given as a function of the total mass needing sedimentation in a given volume. Sedimentation with cationic polymers can yield slurry with solid concentrations over 4 wt%.

Cake filtration performed is quicker than many microfiltration techniques performed on algae cells. It does not require the pore size of the medium to be smaller than the cell, therefore more water is able to migrate through more open area. It only requires that the open space is such that proper algae flocs cannot work through, but water and air flow is hardly constricted. Larger scale filtration of algae biomass is very feasible with low application of pressure. Properly flocculated algae cells can filter with gravity assistance alone. Thin cakes have shorter gravity filtration time. Adding vacuum can decrease the process time from hours to minutes and increase the solids content of the cake by approximately 10-15 wt%. Fortunately, an appropriate filter medium was readily available that could establish a cake and allow vacuum assistance without losing solids. A rate of approximately 0.075 $g/in^2/min$ of dry algae solids can be processed on the 901F filter used. For the various cycle times with one minute of vacuum, a maximum is seen when the feed concentration is at 15 g/L. Without varying feed volume, lower concentration has too much water to evacuate and higher concentration has too thick of

cake for percolation. Both of these inhibitions could possibly be remedied with higher vacuum pressure or added process time.

While this study was useful in acknowledging the possibility of commercial dewatering practices, more work could be done to appropriately size such a system. Continuous harvesting has yet to be studied. Determining the settling velocity of flocs generated with a successful flocculant would be viable research for establishing the design criteria of a gravity thickener. Wall effects could play an important role on the settling behavior of algae biomass. Scalability should be accessed with industrial equipment designed for continuous operation. Gravity thickeners have large diameters with respect to height that could nullify wall effects seen in the lab. Flocculant optimization could be performed, but 10-15 ppm of Zinkan 540 should be very close to the optimal chemical constraints for algae cells.

While this study was performed to better understand how cake filtration could be effective for quickly dewatering algae slurry, it does not go in depth on any of the processing variables that could be obtained from such work. Filtration optimization can be done to select appropriate filter medium that has relatively good airflow specifications, but is still able to capture the pliable algae cells. Selection of filter medium could play an important role in achieving higher throughput. The multifilament, 901F, was able to capture the pliable algae flocs. There are other commercial variations of these types of filters that also incorporate a fabric that is lined with a wire mesh to increase durability over a longer life. Cake discharge and belt washing are two operations that might require investigation. The algae cakes have a tendency of being sticky and adhering to almost anything.

Small scale prototyping might need to be performed to get a better understanding of how this dewatering system would work together. Some general subjects would be effective floc growth with mixing only from fluid transfer during pumping. Inlet discharge turbulence into the gravity thickener may re-suspend flocs. A pilot system may be designed to harvest algae biomass from different sources. This would incorporate a variety of algae strains at different concentrations to assess how reliable the harvesting process would be for this biomass strategy. There is potential for this system as swift, consistent production capacity thickened algae mass for wet utilization or further dried for other purposes.

REFERENCES

Bare, W.F.R., Jones, N.B., and Middlebrooks, E.J. 1975. Algae removal using dissolved air flotation. *Journal Water Pollution Control Federation*. 47(1):153-169.

Benemann, J.R. 1997. CO_2 Mitigation with microalgae systems. *Energy Conversion and Management.* 38:S475-S479.

Chen, Y.M., Liu, J.C., and Ju, Y.H. 1998. Flotation removal of algae from water. *Colloids and Surfaces B: Biointerfaces.* 12(1):49-55.

Crofcheck, C., E, X., Shea, A., Montross, M., Crocker, M., and Andrews, R. 2012. Influence of media composition on the growth rate of *Chlorella vulgaris* and *Scenedesmus acutus* utilized for CO_2 mitigation. *Journal of Biochemical Technology.* 4(2):589-594.

Divakaran, R. and Pillai, S.V.N. 2002. Flocculation of algae using chitosan. *Journal of Applied Phycology.* 14(5):419-422.

EIA 2012. U.S. Energy Information Administration. *Annual Energy Review 2011.* DOE/EIA-0384. September 2012.

EPA 1987. Design manual, dewatering municipal wastewater sludges. *U.S. Environmental Protection Agency*. EPA/625/1-87/014 September:25-36.

EPA 2000a September 2000. *Biosolids Technology Fact Sheet: Belt Filter Press.* U.S. EPA # 832-F-00-057. Washington, D.C. Office of Water.

EPA 2000b September 2000. *Biosolids Technology Fact Sheet: Centrifuge Thickening and Dewatering.* U.S. EPA # 832-F-00-053. Washington, D.C. Office of Water.

EPA 2000c September 2000. *Biosolids Technology Fact Sheet: Recessed-Plate Filter Press.* U.S. EPA # 832-F-00-058. Washington, D.C. Office of Water.

EPA 2003 September 2003. *Biosolids Technology Fact Sheet: Gravity Thickening.* U.S. EPA # 832-F-03-022. Washington, D.C. Office of Water.

EPA 2009. Endangerment and Cause or Contribute Findings for Greenhouse Gases under Section 202(a) of the Clean Air Act. [EPA-HQ-OAR-2009-0171; FRL-9091-8] *Federal Register.* Vol. 74, No. 239. 66496-66546, 2009.

EPA 2012 September 26, 2012. *2012 U.S. Greenhouse Gas Inventory Report.* U.S. EPA # 430-R-12-001. Washington, D.C. Environmental Protection Agency.

Flottweg Separation Technology. 2016. *Flottweg centrifuges for efficient algae harvesting*. https://www.flottweg.com/applications/chemicals-pharmaceuticals-food/algae. Accessed on 20 April 2016.

FLSmidth. 2016. *EIMCO Extractor Horizontal Belt Filter*. http://www.flsmidth.com/~/media/PDF%20Files/Liquid-Solid%20Separation/Filtration/HBF_brochure.ashx. Accessed on 20 April 2016.

Folkman, Y. and Wachs, A.M. 1973. Removal of algae from stabilization pond effluent by lime treatment. *Water Research.* 7(3):419-435.

Friedman, A.A., Peaks, D.A., and Nichols, R.L. 1977. Algae separation from oxidation pond effluents. *Journal of Water Pollution Control Federation.* 49(1):111-119.

Golueke, C.G. and Oswald, W.J. 1965. Harvesting and processing sewage grown planktonic algae. *Journal of Water Pollution Control Federation.* 37(4):47l-498.

Kratz, W.A. and Myers, J. 1955. Nutrition and growth of several blue-green algae. *Journal of Botany*. 42(3):282-287.

Komline-Sanderson. 2016. *Rotary Drum Vacuum Filters*. http://www.komline.com/docs/rotary_drum_vacuum_filter.html. Accessed on 20 April 2016.

Lenntech B.V. 2016. *Filter presses for sludge treatment*. http://www.lenntech.com/library/sludge/presses/filter-press.htm. Accessed on 20 April 2016.

Li, Y., Horsman, M., Wu, N., Lan, C.Q., and Dubois-Calero, N. 2008. Biofuels from microalgae. *Biotechnology Progress*. 24(4):815-820.

Kumar, M.V.R.N. 2000. A review of chitin and chitosan applications. *Reactive and Functional Polymers*. Vol 46(1):1-27.

Mata, T.M., Martins, A.A., and Caetano, N.S. 2010. Microalgae for biodiesel production and other application: A review. *Renewable and Sustainable Energy Reviews.* 14(1):217-232.

McGarry, M.G. 1970. Algae flocculation with aluminum sulfate and polyelectrolytes. *Journal of Water Pollution Control Federation.* 42(5):R19l-R201.

Moraine, R., Shelef, G., Sandbank, E., Bar Moshe, Z., and Schwarbard, L. 1980. Recovery of sewage born algae: Flocculation and centrifugation techniques. In: Shelef, G. and Soeder, C.J. (Eds). *Algae Biomass: Production and Use*. Amsterdam-New York-Oxford: Elsevier/North-Holland Biomedical Press, 531-546.

Nigam, B.P., Ramanathan, P.K., and Venkataraman, L.V. 1980. Application of Chitosan as a flocculant for the cultures of the green-alga – *Scenedesmus Acutus*. *Archiv fur Hydrobiologie.* 88(3):378-387.

Noue, J.D.L. and Pauw, N.D. 1988. The potential of microalgal biotechnology: A review of production and uses of microalgae. *Biotechnology Advanced.* 6(4):725-770.

Pulz, O. and Gross, W. 2004. Valuable products from biotechnology of microalgae. *Applied Microbiology and Biotechnology.* 65(6):635-648.

Shamlou, P.A., ed. 1993. *Processing of Solid-Liquid Suspensions.* Oxford, Butterworth-Heineman, Ltd.

Shelef, G., Sukenik, A., and Green, A. 1984. Microalgae harvesting: A literature review. SERI/STR-231-2396, UC Category: 61a, DE84013036.

Sim, T.S., Goh, A., and Becker, E.W. 1988. Comparison of centrifugation, dissolved air flotation and drum filtration techniques for harvesting sewage-grown algae. *Journal of Biomass.* 16(1):51-62.

Somasundaran, P. 1980. Principles of flocculation, dispersion, and selective flocculation. In: Fine Particle Processing: Proceedings of the International Symposium on Fine Particles Processing, Las Vegas, Nevada, February 24-28, v2. New York, NY: American Institute of Mining, Metallurgical, and Petroleum Engineers, 947-976.

Spicer, P.T., Keller, W., and Pratsinis, S.E. 1996. The Effect of Impeller Type on Floc Size and Structure during Shear-Induced Flocculation. *Journal of Colloid and Interface Science.* 184(1):112-122.

Stechemesser, H. and Dobias, B. Eds. 2005. *Coagulation and Flocculation* (2nd ed.). Boca Raton: CRC Press.

Stensel, H.D, Tsuchihashi, R., Tchobanoglous, G., Arthur, J., and Franklin, B. 2013. Wastewater Engineering: Treatment and Resource Recovery. Fifth edition. The McGraw Hill Companies, 2 Penn Plaza, New York, NY 10121.

Sukenik, A., Bilanovic, D., and Shelef, G. 1988. Flocculation of microalgae in brackish and sea waters. *Biomass.* 15(3):187-199.

Tenney, M.W., Echelberger, W.F., Schuessler, R.G., and Pavoni, J.L. 1969. Algal flocculation with synthetic organic polyelectrolytes. *Applied Microbiology.* 18(6):965-971.

Uduman, N., Qi, Y., Danquah, M.K., Forde, G.M., and Hoadley, A. 2010. Dewatering microalgal cultures: A major bottleneck to algae-based fuels. *Journal of Renewable Sustainable Energy.* 2(1):1-15.

Vandamme, D., Pontes, S.C.V., Goiris, K., Foubert, I., Pinoy, L.J.J., and Muylaert, K. 2011. Evaluation of electro-coagulation-flocculation for harvesting marine and freshwater microalgae. *Biotechnology and Bioengineering.* 108(10):2320-2329.

Vandamme, D., Foubert, I., Fraeye, I., Meesschaert, B., and Muylaert, K. 2012. Flocculation of *Chorella vulgaris* induced by high pH: Role of magnesium and calcium and practical implications. *Bioresource Technology*. 105:114-119.

Vernick, A.S. and Walker. E.C., Eds. 1981. *Handbook of Wastewater Treatment Processes*. New York: Marcel Dekker, Inc.

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